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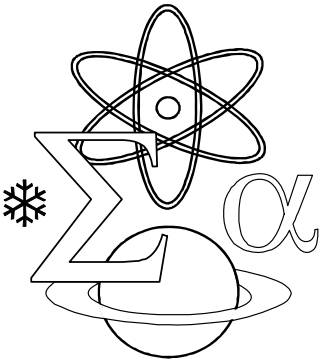

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This Journal is a multidisciplinary publication devoted to all field of Natural and Technical Sciences. The Editor of JNTS invites original contributions which should comprise previously unpublished results, data and interpretations. Types of contributions to be published are: (1) research papers; (2) shorts communications; (3) reviews; (4) discussions; (5) book reviews; (6) annonuncements.

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GREEN'S RELATIONS $\mathcal{H}$ AND $\mathcal{Q}$ IN RINGS

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ABSTRACT

In this paper, firstly we show certain relations that hold between the equivalence classes of the relations $\mathcal{H}$ and $\mathcal{Q}$ in a ring $(A,+,\cdot)$ and the respective equivalence classes of the Green's relations $\mathcal{H}(\cdot)=\mathcal{Q}(\cdot)$ defined on the multiplicative semigroup $(A,\cdot)$ of this ring. Further, using these relations we study a case when a minimal quasi-ideal of the ring $(A,+,\cdot)$ is again minimal regarded as a quasi-ideal of the multiplicative semigroup $(A,\cdot)$ of this ring and we find another proof of Green's theorem for rings. Lastly, we study the behavior of a ring, which does not have the identity element and zero divisors, regarding relations $\mathcal{H}$ and $\mathcal{Q}$. Also, we discuss the case when two non-zero elements of a ring are $\mathcal{H}$ and consequently $\mathcal{Q}$ equivalent.
Keywords: ring, division ring, semigroup, left ideal, right ideal, Green's relations

1. INTRODUCTION

By a ring we mean an associative ring, which does not necessary have an identity element. The Green's relation $\mathcal{H}$ and the relation $\mathcal{Q}$ in the rings are introduced and studied by Petro (1981; 2002). These relations mimic the relations $\mathcal{H}$ in semigroups which is introduced and studied for the first time by James Aleksander Green (Green, 1951) and also the relation $\mathcal{Q}$ in semigroups for which it is shown that $\mathcal{H}=\mathcal{Q}$ (Steinfeld, 1978). This is the reason that the relations $\mathcal{H}$ and $\mathcal{Q}$ in rings are called Green's relations. Generally, in contrast to semigroups it is shown that $\mathcal{H}\neq\mathcal{Q}$ in a ring although we always have $\mathcal{Q}\subseteq\mathcal{H}$. We will denote by $\mathcal{H}$ and $\mathcal{Q}$ the Green's relations in a ring $(A,+,\cdot)$, meanwhile the Green's relations in the multiplicative semigroup $(A,\cdot)$ of this ring will be denoted by $\mathcal{H}(\cdot)$ and $\mathcal{Q}(\cdot)$ to be distinguished from those of the ring $(A,+,\cdot)$. These two kinds of relations are determined by the equalities of the principal left ideals and the principal right ideals and the equalities of the principal quasi-ideals of the ring $(A,+,\cdot)$ and it's multiplicative semigroup $(A,\cdot)$. Firstly, in this paper we show relation that exists between the equivalence classes under the Green's relations $\mathcal{H}$ and $\mathcal{Q}$ of a ring and the respective equivalence classes under the relations $\mathcal{H}(\cdot)$ and $\mathcal{Q}(\cdot)$ of the multiplicative semigroup of this ring. Further, by using these

relations we show a sufficient condition for a minimal quasi-ideal of a ring to remain minimal in the multiplicative semigroup of this ring. Lastly, we study Green's relations $\mathcal{H}$ and $\mathcal{Q}$ in rings, which do not have an identity element and divisors of zero. In the end of this paper we raise an open problem.

2. **Preliminaries**

We give some notions and present some auxiliary results that will be used throughout the paper.

Let $(A, +, \cdot)$ be a ring and *B*, *C* two subsets of *A*. We write:

$$B + C = \{b + c \in A : b \in B, c \in C\},$$
$$BC = \{\sum_{i=1}^{n} b_i c_i \in A : \ b_i \in B, c_i \in C\}.$$

For simplicity we will write bC instead of $\{b\}C$ and Bc instead of $B\{c\}$.

By a quasi-ideal (Steinfeld, 1978) [left ideal, right ideal] of a ring $(A, +, \cdot)$ we shall mean a subgroup Q $[L, R]$ of the additive group $(A, +)$ of this ring such that $Q \cap QA \subseteq Q$ $[AL \subseteq L, RA \subseteq R]$.

It is not difficult to show that the intersection of all quasi-ideals [left ideals, right ideals], which contain the element $a \in A$ is a quasi-ideal [left ideal, right ideal] of A and it is denoted by $(a)_q$ $[(a)_l, \ (a)_r]$ and it is called the principal quasi-ideal [left ideal, right ideal] generated by the element $a \in A$. Further, the following equalities are true:

$$(a)_l = \mathbb{Z}a + Aa, \tag{2.1}$$
$$(a)_r = \mathbb{Z}a + aA, \tag{2.2}$$
$$(a)_q = \mathbb{Z}a + aA \cap Aa. \tag{2.3}$$

The Green's relations $\mathcal{H}$ and $\mathcal{Q}$ in a ring A (Petro, 2002) are defined as follows:

$$\forall (a, b) \in A^2, a\mathcal{H}b \Leftrightarrow [(a)_l = (b)_l \ \wedge \ (a)_r = (b)_r \ ],$$
$$\forall (a, b) \in A^2, aQb \Leftrightarrow (a)_q = (b)_q,$$

The relations $\mathcal{H}$ and $\mathcal{Q}$ in a ring A are equivalent relations. The equivalence class $mod\mathcal{H}$ and the equivalence class $modQ$ containing the element *a* of *A* are denoted by H_a and Q_a respectively.

If in the above definitions of Green's relations $\mathcal{H}$ and Q in the ring *A*, we replace the ring *A* with an arbitrary semigroup *S* and the principal left ideals, principal right ideals and principal quasi-ideals we regard as principal left ideals, principal right ideals and principal quasi-ideals of semigroup *S*, then

we have Green's relations in the semigroup S, which we will denote by the same symbol as Green's relations in the ring A. In this paper, to distinguish between the Green's relations $\mathcal{H}$ and $\mathcal{Q}$ in the ring $(A,+,\cdot)$ from the Green's relations in the multiplicative semigroup $(A,\cdot)$ of this ring, these latter ones are denoted by $\mathcal{H}(\cdot)$ and $\mathcal{Q}(\cdot)$. Also, the equivalence classes of the element a of the multiplicative semigroup $(A,\cdot)$ of the ring $(A,+,\cdot)$ under the Green's relations $\mathcal{H}(\cdot)$ and $\mathcal{Q}(\cdot)$ are denoted by $H_a(\cdot)$ and $Q_a(\cdot)$.

Theorem 2.1. (Sema and Petro 2014) Let $(A,+,\cdot)$ be a ring and a an element of A. Then the $\mathcal{L}[\mathcal{R}]$-class L_a $[R_a]$ is either a union of $\mathcal{L}(\cdot)$-classes $[\mathcal{R}(\cdot)$-classes] of the multiplicative semigroup $(A,\cdot)$ of the ring $(A,+,\cdot)$, which must have a single element, or $L_a = L_a(\cdot)$ $[R_a = R_a(\cdot)]$.

Theorem 2.2. (Cliford and Priston 1961) If a, b, ab all belong to the same $\mathcal{H}$-class H of a semigroup S, then H is a subgroup of S.

Proposition 2.3. (Howie 1995). Let S be a cancellable semigroup (that is a semigroup in which, for all a,b,c, $ca = cb \Longrightarrow a = b$ and $ac = bc \Longrightarrow a = b$) and suppose that S has not an identity. Then $\mathcal{L} = \mathcal{R} = 1_A$.

3. **Main results**

Let $(A,+,\cdot)$ be an arbitrary ring. As previously stated we consider the Green's relations $\mathcal{H}$ and $\mathcal{Q}$ in the ring $(A,+,\cdot)$ and the Green's relations $\mathcal{H}(\cdot)$ and $\mathcal{Q}(\cdot)$ in the multiplicative semigroup $(A,\cdot)$ of this ring. If the ring $(A,+,\cdot)$ has an identity element, then from the equalities (2.1), (2.2) and (2.3) follows immediately that $\mathcal{H} = \mathcal{H}(\cdot)$ and $\mathcal{Q} = \mathcal{Q}(\cdot)$. In general, from the equalities (2.1), (2.2) and (2.3) it is obvious that $\mathcal{H}(\cdot) \subseteq \mathcal{H}$ and $\mathcal{Q}(\cdot) \subseteq \mathcal{Q}$.

The following example shows that these inclusions may be strict ones.

Example 3.1. Let S be a semigroup with zero. We write $\mathbb{Z}[S]$ for the semigroup ring over the ring of integers $\mathbb{Z}$. It is not difficult to see that for every element $a \in S \subseteq \mathbb{Z}[S]$ we have:

$$-a \in H_a, -a \in \mathcal{Q}_a, -a \notin H_a(\cdot), -a \notin \mathcal{Q}_a(\cdot).$$

This example also shows in general the Green's relations $\mathcal{H}$ and $\mathcal{Q}$ in a ring are different from Green's relations $\mathcal{H}(\cdot)$ in the multiplicative semigroup of this ring. So, the Green's relations in a ring that we study in this paper are different from Green's relations in a ring defined as Green's relations in its respective semigroup (Nai-feng, 2002).

Theorem 3.2. Let $(A,+,\cdot)$ be a ring and a an element of A. Then the $\mathcal{H}$-class H_a is either a union of $\mathcal{H}(\cdot)$-classes of the multiplicative semigroup $(A,\cdot)$ of the ring $(A,+,\cdot)$, which must have a single element, or $H_a = H_a(\cdot)$.

Proof. There are two possible cases:

Case 1. Every $H_x(\cdot)$ class, which is inclused in H_a has only one element. Then we have:

$$H_a = \bigcup_{x \in H_a} H_x(\cdot).$$

Case 2. There is one class $H_x(\cdot)$, $x \in H_a$, which has at least two elements. Let b and c be two different elements of A, which belong to $H_x(\cdot)$. Since

$$L_x(\cdot) \cap R_x(\cdot) = H_x(\cdot) \subseteq H_a = L_a \cap R_a,$$

the elements a, b different from each other belongs to $L_x(\cdot)$, $R_x(\cdot)$, $L_a(\cdot)$ and $R_a(\cdot)$ at the same time.

So, from **Theorem 2.1** we have $L_a = L_a(\cdot)$ and $R_a = R_a(\cdot)$. From these two equalities we have the following equalities:

$$H_a = L_a \cap R_a = L_a(\cdot) \cap R_a(\cdot) = H_a(\cdot). \qquad \blacksquare$$

Theorem 3.3. Let $(A,+,\cdot)$ be a ring and a an element of A. If $a^2 \in H_a$, then $H_a = H_a(\cdot)$.

Proof. Suppose that $a^2 \in H_a$. Let x be an element of the class $H_a = H_{a^2}$. Then there exist integers k, k_1 and the elements u, u_1 of A such that:

$$a = kx + ux \text{ and } x = k_1 a^2 + u_1 a^2.$$

From this we have the equalities:

$$x = k_1 a^2 + u_1 a^2 = (k_1 a + u_1 a)a = (k_1 a + u_1 a)(kx + ux) =$$
$$= (k_1^2 ka + k_1 kau_1 + k_1^2 au + k_1 auu_1 + kk_1 u_1 a + ku_1 au_1 + k_1 u_1 au +$$
$$u1auu1a2.$$
$$a^2 = a(kx + ux) = (ka + au)x,$$

that show $x\mathcal{L}(\cdot)a^2$. In the same way we prove that $x\mathcal{R}(\cdot)a^2$. So for every element x of H_a we have $x\mathcal{H}(\cdot)a^2$ and consequently, $H_a = H_a(\cdot)$.■

Now we will prove the Green's theorem for rings (Petro 2002) without using the Green's lemma (Steinfeld 1988; Petro 2002).

Theorem 3.4. [The Green's theorem for rings]. If the elements a, b, ab of the $(A, +, \cdot)$ belong to the same $\mathcal{H}$-class H of this ring, then H is a subgroup of the multiplicative semigroup $(A, \cdot)$ of the ring $(A, +, \cdot)$.

Proof. There are two possible cases.

First case. The elements a, b are equal. Then we have $ab = a^2 \in H_a = H$. From **Theorem 3.3** we have $H = H_a = H_a(\cdot)$. Since it is evident that the elements a, a^2 belong $H_a(\cdot)$, then H is a subgroup of the multiplicative semigroup of the ring $(A, +, \cdot)$ by Green's theorem for semigroups (**Theorem 2.2**).

Second case. The elements a, b are different to each other. Since the elements a, b belong the $\mathcal{H}$-class H, then there exist the integers k_2, k_3, k_4, k_5 and the elements u_2, u_3, u_4, u_5 of A such that:

$$b = k_2a + u_2a,\ b = k_3ab + u_3ab,\ a = k_4ab + u_4ab.$$

From these we have the following equalities:

$$\begin{aligned} b = k_3ab + u_3ab = (k_3a + u_3a)b &= (k_3a + u_3a)(k_2a + u_2a) \\ &= (k_3k_2a + k_3au_2 + k_2u_3a + u_3au_2)a, \\ a = k_4ab + u_4ab &= (k_4a + u_4a)b, \end{aligned}$$

which show that $a\mathcal{L}(\cdot)b$. In the same way we prove $a\mathcal{R}(\cdot)b$. So, $a\mathcal{H}(\cdot)b$ and from **Theorem 3.2** the $\mathcal{H}$-class $H = H_a$ coincide with $\mathcal{H}(\cdot)$ class $H_a(\cdot)$. From Green's theorem for semigroups (**Theorem 2.2**) H is a subgroup of the multiplicative semigroup $(A, \cdot)$ of the ring $(A, +, \cdot)$.■

The analogue theorems of the theorems 3.2 and 3.3 are true for the relation Q.

Theorem 3.5. Let $(A, +, \cdot)$ be a ring and a an element of A. Then the Q-class Q_a is either a union of $Q(\cdot)$-classes of the multiplicative semigroup $(A, \cdot)$ of the ring $(A, +, \cdot)$, which must have a single element, or $Q_a = Q_a(\cdot)$.

Proof. There are two possible cases:

Case 1. Every $Q_x(\cdot)$ class, which is includes in Q_a has only one element. Then we have:

$$Q_a = \bigcup_{x \in Q_a} Q_x(\cdot).$$

Case 2. There is one class $Q_x(\cdot)$, $x \in Q_a$, which has at least two elements. Let b and c be two different elements of A, which belong to $Q_x(\cdot)$. From **Theorem 3.2** we have:

$$Q_a(\cdot) \subseteq Q_a \subseteq H_a = H_a(\cdot) = Q_a(\cdot).$$

and consequently $Q_a = Q_a(\cdot)$. ■

Theorem 3.6. Let $(A, +, \cdot)$ be a ring and a an element of A. If $a^2 \in Q_a$, then $Q_a = Q_a(\cdot)$.

Proof. From **Theorem 3.3** we have:

$$Q_a(\cdot) \subseteq Q_a \subseteq H_a = H_a(\cdot) = Q_a(\cdot),$$

and consequently $Q_a = Q_a(\cdot)$.■

Since, in the multiplicative semigroup $(A, \cdot)$ of the ring $(A, +, \cdot)$ we have the equality $\mathcal{H}(\cdot) = Q(\cdot)$ it is not difficult to adapt the proof of **Theorem 3.5** in order to produce a proof for the following theorem, which resemble with Green's theorem for rings that is proven in another way by (Petro, 2002).

Theorem 3.7. If the elements a, b, ab of the ring $(A, +, \cdot)$, which belong to the same Q-class Q of A, then Q is a subgroup of the multiplicative semigroup $(A, \cdot)$ of the ring $(A, +, \cdot)$.

Definition 3.8. Two elements a, b of the ring A are called divisors to each other if there are elements c_1, c_2, c_3, c_4 of A such that :

$$a = c_1 b, b = c_2 a, a = b c_3, b = a c_4.$$

Proposition 3.9. If the minimal quasi-ideal Q of the ring $(A, +, \cdot)$ has two different elements, which are divisiors to each other, then Q is a minimal quasi-ideal of the multiplicative semigroup $(A, \cdot)$ of the ring $(A, +, \cdot)$.

Proof. Since Q is a minimal quasi-ideal, there exists an element $a \in Q$ such that $Q = (a)_q$. Let b, c be two element of Q, which are divisiors to each other. So, $bQ(\cdot)c$. From **Theorem 3.5** the following equalities hold true:

$$(a)_q = Q_a \cup 0 = Q_a(\cdot) \cup 0.$$

On the other hand if we write a_q^S for the principal quasi-ideal of the multiplicative semigroup $(A,\cdot)$ of the ring $(A,+,\cdot)$, which is generated by the element $a \in A$, we have:

$$Q_a(\cdot) \cup 0 \subseteq (a)_q^S \subseteq (a)_q = Q_a(\cdot) \cup 0.$$

So,

$$(a)_q = (a)_q^S = Q_a(\cdot) \cup 0.$$

Now, it is clear that the minimal quasi-ideal Q of the ring $(A,+,\cdot)$ regarded as a quasi-ideal of semigroup $(A,\cdot)$ is minimal. ■

If a $\mathcal{H}$-class [Q-class] H_a [Q_a] of the ring has only one element, then it is clear that $H_a = H_a(\cdot)$ [$Q_a = Q_a(\cdot)$]. The following proposition gives a case when the only classes $mod\mathcal{H}$ and $mod\ Q$ of the ring $(A,+,\cdot)$ coincide with the respective classes $mod\ \mathcal{H}(\cdot)$ and $mod\ Q(\cdot)$ of the multiplicative semigroup $(A,\cdot)$ of this ring are those which have only one element.

Proposition 3.10. Let $(A,+,\cdot)$ be a ring, which has at least two elements but it does not have an identity element and divisors of zero. Then the only classes $mod\ \mathcal{H}$ [$mod\ Q$] in the ring $(A,+,\cdot)$ that coincide with the respective classes $mod\ \mathcal{H}(\cdot)$ [$mod\ Q(\cdot)$] in the multiplicative semigroup of this ring are those which have only one element.

Proof. Since the ring $(A,+,\cdot)$ does not have divisors of zero, then the set $A^* = A\backslash 0$ is closed under the multiplication of the ring A and forms a semigroup with respect to the multiplication induced in it. It is clear that the semigroup $(A^*,\cdot)$ does not have an identity element and it is a cancelable semigroup. We see that for every element $a \neq 0$ of A, the class $H_a(\cdot)$ of the element a of the semigroup $(A,\cdot)$ has only one element by **Proposition 2.3**. From **Theorem 3.2** we have $H_a = H_a(\cdot)$ if and only if H_a has only one element. The proof for the relation Q is similar with the only change that in place of **Theorem 3.2** we use **Theorem 3.5.** ■

From this proposition we have the following corollary:

Corollary 3.11. In a ring $(A,+,\cdot)$, which does not have an identity element and divisors of zero the Green's relations $\mathcal{H}$ and Q coincide with Green's relation $\mathcal{H}(\cdot)$ of the multiplicative semigroup $(A,\cdot)$ of this ring and consequently $\mathcal{H} = Q$ if and only if $\mathcal{H} = 1_A$, where 1_A is the identity relation in A.

Above we saw an extreme case when Green's relations $\mathcal{H}$ and Q in a ring are the finest possible, which means that the equivalence class $mod\mathcal{H}$ and the equivalence class $modQ$ has only one element.

Now, we will examine another extreme case, precisely the case when the Green's relations in a ring are the thickest possible, i.e. when every two non-zero elements of a ring are equivalent under this relations. In this case it is clear that for every $a \in A\backslash 0$, we have $H_a = Q_a = A\backslash 0$. When this happens we say that the ring A is $\mathcal{H}$-simple [Q-simple].

In fact, it is clear that, when a ring A is Q-simple, then it is $\mathcal{H}$-simple, since $Q \subseteq \mathcal{H}$.

From Green's theorem for rings (**Theorem 3.4**) follows immediately that a nonzero ring A is $\mathcal{H}$-simple, and then it is a field. So, if a nonzero ring $(A,+,\cdot)$ is $\mathcal{H}$-simple [Q-simple], then the Green's relation $\mathcal{H}$ coincide with Green's relation $\mathcal{H}(\cdot) = Q(\cdot)$ in the multiplicative semigroup $(A,\cdot)$ of this ring and furthermore we have $\mathcal{H} = Q$.

Conversely, if the multiplicative semigroup $(A,\cdot)$ of the ring $(A,+,\cdot)$ has at least two elements the only $\mathcal{H}(\cdot) = Q(\cdot)$ classes are 0 and $A\backslash 0$, then it is clear that the ring $(A,+,\cdot)$ is $\mathcal{H}$-simple [Q-simple].

So, in the second extreme case, when the Green's relations $\mathcal{H}$ and Q in a ring $(A,+,\cdot)$ are trivial, then they coincide with the respective Green's relations in the multiplicative semigroup $(A,\cdot)$ of this ring and vice-versa. While in the first extreme case, we saw that this equality does not hold (we saw a special case when we have this equality).

So, it is natural to raise the following problem.

Problem. Find necessary conditions, sufficient conditions, necessary and sufficient conditions, so that if in the ring $(A,+,\cdot)$ the Green's relation $\mathcal{H}(\cdot) = Q(\cdot)$ in the multiplicative semigroup $(A,\cdot)$ of this ring is the identity relation 1_A, then the relation $\mathcal{H}$ [Q] is equal to 1_A.

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QUALITY CONTROL OF NUCLEAR MEDICINE AT THE UNIVERSITY HOSPITAL CENTER, TIRANA

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ABSTRACT

Daily, weekly, monthly and annual different tests have been carried out at the Department of Nuclear Medicine, University Hospital Centre in Tirana, Albania for the quality control of gamma camera and the results are here reported. The duration of the tests varied from 20 minutes for the peak power test, up to 1 hour which is the annual test for the uniformity of the system. The results reported a good performance of the gamma camera.

Key words: quality control, gamma camera, nuclear medicine.

1. INTRODUTION

Quality control in nuclear medicine provides the proper functioning of different devices, like gamma camera and ensures the integrity of the diagnostic image produced. The parameters most commonly evaluated for routine gamma-camera include the physical parameters such as spatial and energy resolution, spatial linearity and uniformity etc., which help obtain a good quality image (OMS 1983).

The present investigation aims at evaluating: i) the physical parameters, ii) quality control instrumentation and, iii) the standard protocol applied by physicians to investigate the two aforementioned parameters (Grahman 1988).

Nuclear Medicine imagery presents particular advantages in diagnosing a variety of diseases, malignant or not. For this physicians should constantly have available tools that make it possible to implement a safe diagnosis with consistent quality (Anger 1958).

Regularly performed protocols help set up the quality assurance programs which relate with all the aspects of nuclear medicine diagnostic efforts, and include evidence of regular quality controls of the equipments (Webb 2000). The concept of quality assurance deals with the overall diagnostic process from radiopharmaceutical management to the examination report of course passing the equipment (AAPM Report No. 6). Quality control is performed with different devices intended to take the best result possible which includes supervising, evaluating and maintaining an optimum level of all characteristics that can be measured and regulated.

Quality control of gamma-camera constitutes a fundamental issue of this program and the implementation of which ought to be carried out by qualified personnel, according to the Decision/Order of 8 August 1988, referring to the European Directive 13 September 1984 concerning the radiological protection of patients (Johansson 2003).

Scintillation gamma-camera is a basic equipment of nuclear medicine services. Tests of physical parameters provide optimisation of device imagining and importance of possible damages.

IAEA (1991) recommended that tests should be reproducible, easy to implement, fast and easy in execution and in line with a good predetermined protocol. In addition, simple equipments have to be used in order to remain close to the conditions of clinical use providing at the same time essential information regarding the physical parameters of the devise.

2. METHOD AND MEASUREMENTS

Different parameters were tested based on the recommendations of IAEA (2003).

2.1. The own uniformity

The collimators were removed due to lack of own uniformity and the radioactive source ^{99m}Tc, with activity 37 MBq placed in a holder of Pb which is positioned in the centre of the detectors was used. The distance between source and detector was 20 cm. The matrix that was used had maximum size 1024×1024. Spectral window was centred ±10% in the total absorption peak and the counting speed was 100000 imp/s. This is a weekly test that lasts 1 an hour. These parameters together with the data and type of test were registered in the software. One hour later, an image of 30 million events in the format 1024×1024 detectors was obtained for both detector (Fig. 1).

2.2. The integral uniformity U_i and U_d

For detector 1 lack of integral and differential uniformity are as follows:

- Lack of integral uniformity U_i is:

$$U_{i_1} = \pm 100 \frac{V_M - V_m}{V_M + V_m} = 5.72\% \qquad \text{for CFOV (Central Field of View)}$$

$$U_{i_1} = \pm 100 \frac{V_M - V_m}{V_M + V_m} = 6.31\% \qquad \text{for UFOV (Useful Field of View)}$$

- Lack of differential uniformity U_d is:

$$U_{d_1} = \pm 100 \frac{V_s - V_i}{V_s + V_i} = 3.76\% \qquad \text{for CFOV}$$

$$U_{d_1} = \pm 100 \frac{V_s - V_i}{V_s + V_i} = 3.76\% \qquad \text{for UFOV}$$

For detector 2 lack of integral and differential uniformity are :

- Lack of integral uniformity U_i is :

$$U_{i_2} = \pm 100 \frac{V_M - V_m}{V_M + V_m} = 5.76\% \text{ for CFOV}$$

$$U_{i_2} = \pm 100 \frac{V_M - V_m}{V_M + V_m} = 5.76\% \text{ for UFOV}$$

- Lack of differential uniformity U_d is: (Aubert *et al*., 1991)

$$U_{d_2} = \pm 100 \frac{V_s - V_i}{V_s + V_i} = 3.93\% \text{ for CFOV}$$

$$U_{d_2} = \pm 100 \frac{V_s - V_i}{V_s + V_i} = 3.93\% \text{ for UFOV}$$

2.3. The own spatial resolution

Here, the collimators were removed and the radioactive source ^{99m}Tc with activity 100 MBq placed in a holder of Pb which is positioned in the centre of the detectors was used. The distance between source and detector is 20cm. A matrix 256x256 in size and with many cracks (Fig. 6) is used for energy 145 keV. The source was placed in such position to cover the entire view field of the detector without collimator. The matrix was orientated in such a way that the axis of the cracks was perfectly directed according to the electronic axis X and then Y. As the restrictive field was limited, the cover of areas was beyond the view field. Spectral window is centred ± 10% in the total absorption peak and counting speed is 200000 imp/s. This is a monthly and annual test that lasts 30 min-1hr. These parameters together with the data and type of test are registered in the software. An image of 100 events in the format 256 x 256 for 2 detectors is obtained (Fig. 4). The evaluation of spatial resolution is made directly from software (Table. 3).

2.4. The spatial system resolution

Here the radioactive source ^{99m}Tc with activity 100 MBq is used. Spectral window is centred ±10% on total absorption peak, while counting speed is 20000 imp/s. This test involved the matrix comprising a set of tiles made of plexiglass with width 1-5 cm and dimensions 30 cm x 30cm. One of these tiles is eroded to fix the flexible pipes —with internal diameter 0.5mm—that can be filled with ^{99m}Tc radioelement. The formed linear sources are placed perpendicular to the axis of collimator customized with radioelement energy which is 140 keV and parallel to one of the detector electronic axis X or Y. Air area between the entry side of collimator and phantom surface is about 15 cm thick. For this distance an image is taken (Fig. 5) in the smallest available escalation. Maximal pixel contains at least 100 events. Both detector axis are explored. The obtained images are examined and the minimal space between 2 sources was marked, the images of sources are visually separated. Test frequency is every year and lasts 1 hour. The evaluation of spatial resolution is made directly from the software (Table. 4).

2.5. The own spatial linearity

Images taken from own spatial resolution test (Fig. 5) are used due to the lack of own spatial linearity test, too, according to X and Y axis. It is an annual test that lasts 1 hour (Gibson 1992).

2.5.1. The differential spatial linearity

In the present investigation the phantom with cracks (Fig. 3 are used to create the profiles starting from strips perpendicular to the axis of cracks and

with a width equal to 30 mm in the direction of these axes. Straps are next to each other. X_E location of each peak is determined based on the half-heights obtained by interpolation $X_E = (X_A + X_B)/2$=140keV. In every stripe the distances between neighbouring peaks positions are set. Lack of differential spatial linearity, for the view field of the detector is the standard deviation of all distances measured in "mm" to images obtained (Table.5) by X and Y directions (Fig. 3). Conversion factor mm/pixel is obtained by dividing the actual distance between two neighbouring peaks (30 mm) with average distances measured in pixels, for all peaks of the detector view field.

2.5.2. The absolute spatial linearity

The absolute spatial linearity could be obtained using the smallest squares method, 2 series of data obtained separately by X and Y in a set of parallel lines equally spaced between neighbouring peaks, by the reviewed orientation. It appears from the largest value in mm of X and Y displacement between observed lines and adjusted in the entirety view field of the detector (Fig.4 , Table.6).

2.6. The linearity spatial of the system

Here, the radioactive source ^{99m}Tc with activity 370 MBq is used. Spectral window is centred in the total absorption peak, while counting speed is 15000 imp/s. A phantom with cracks was used with spatial resolution (Fig. 6) together with the size of the detector with collimator. The source was put on the phantom which is about 15 cm from collimator adapted to the radiation energy, where was explored the two X and Y directions. The test frequency is annual and the test duration is 40 min. As a result was g an image at 256×256 format. The maximum pixel content must be greater than 100 events. Images obtained (Fig. 4, Table 6) are visualized and monitored in each of the document exit devices.

2.7. The energy resolution

The radioactive source ^{99m}Tc with activity 100 MBq placed in a holder of Pb which is placed in the centre of the detectors is used for the energy resolution. The distance between source and detector is 20cm. The matrix used is 256x256. Spectral window is centred on total absorption peak and the counting speed is 100000 imp/s. It is a weekly test that lasts 30 min. As result is obtained an energy spectre in the best available escalation (Fig. 5). The channel content that corresponds to maximal total absorption peak, must be greater than 10000. When this was necessary we escalated the channels by energy, using a second radioelement with approximate energy; for example

^{57}Co. Own energy resolution corresponds to the width at half-height of the total absorption peak expressed as a percentage of the energy reviewed. (Table 7)

3. RESULTS AND DISCUSSION

Below are shown the results of the measurements represented through Figures 1-5 and Tables 1-7.

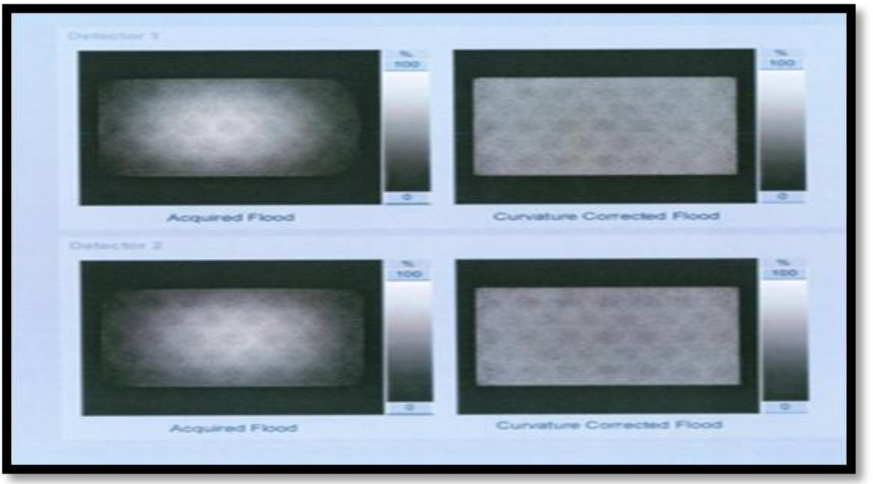

Fig.1. Lack of own uniformity.

Table.1 Results for pixel values for UFOV and CFOV

	UFOV	**CFOV**
Average pixel value	12373	12370
Maximal pixel value	12591	12591
Minimal pixel value	12135	12135

UFOV

Table.2 Own spatial resolution test results

	X(mm)	**Y(mm)**	**AVEREG (mm)**
GJL	2.93	2.90	5.91
GJDL	5.71	5.64	5.67

CFOV

Table 3 Own spatial resolution test results

	X(mm)	**Y(mm)**	**AVEREG (mm)**
GJL	2.87	2.83	2.85
GJDL	5.60	5.51	5.56

Table 4 System spatial resolution test results

	X(mm)	**Y(mm)**
GJL	6.60	7.68
GJDL	12.30	13.88

Table 5 Lack of absolute spatial linearity

	Size (pixel)	**Size (mm)**
Standard deviation by Y	0.07	0.15
Standard deviation by X	0.09	0.19

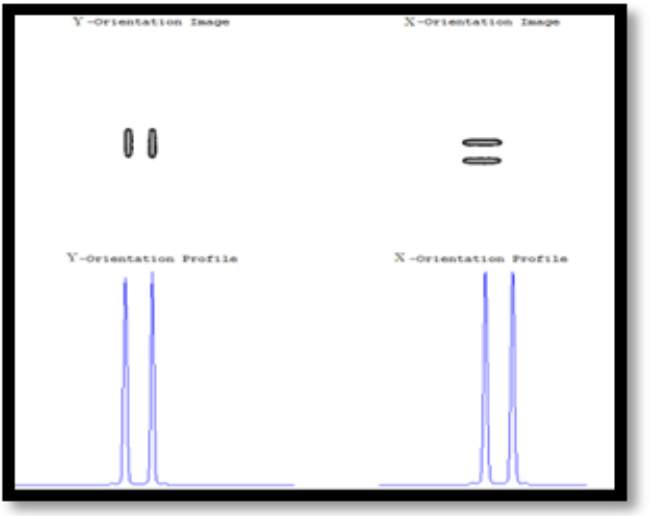

Fig.2 System spatial resolution.

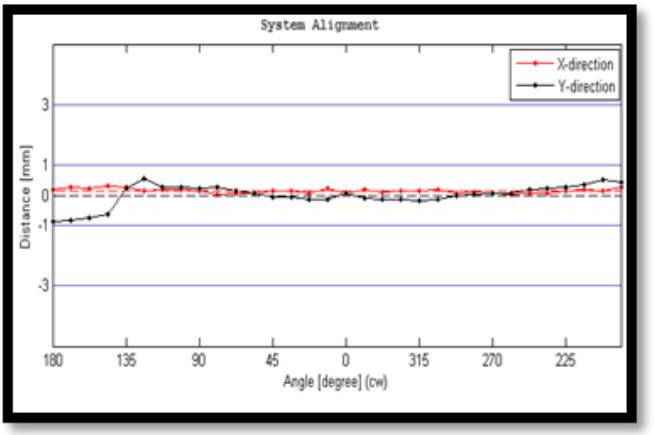

Fig 3. Lack of differential spatial linearity.

Table 6. Lack of differential spatial linearity test results

	Size (pixel)	**Size (mm)**
Standard deviation by Y	0.42	0.86
Standard deviation by X	0.08	0.17

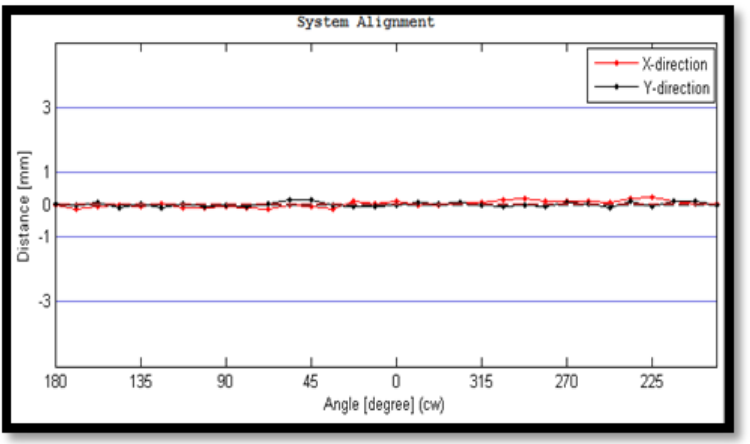

Fig. 4. Lack of absolute spatial linearity and system spatial linearity.

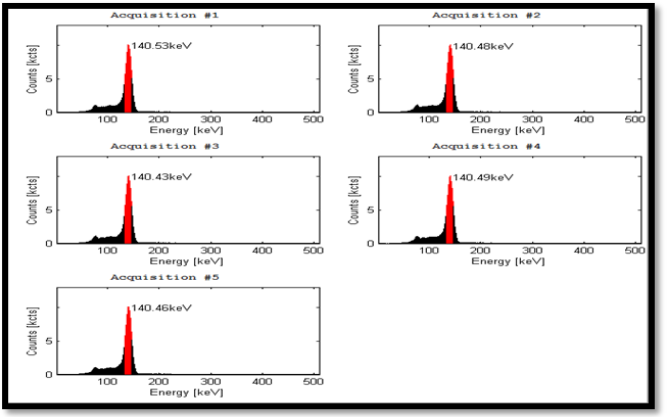

Fig. 5. Energy resolution.

Table.7 GJL values calculated from devises software for every peak

GJL value No.1 GJL value No.2	9.20% 9.30%
GJL value No.3	9.31%
GJL value No.4	9.04%
GJL value No.5	9.41%
GJL average value	9.25% ± 0.01%

By the values given in the above tables and figures it is seen that the main parameter of gamma camera are in good accordance with installed parameters.

4. CONCLUSIONS

Image quality depends on the distance source-collimator and the protocol used. The distance between the source and collimator goes up to 20 cm.

Quality of image is obtained using the correction systems of uniformity, linearity and energy resolution.

For each test is needed the source with its corresponding activity, collimators or not, type of matrix with dimensions 256x256 to the maximum extent 1024x1024, these parameters change from one test to another. Performed tests are lack of uniformity, spatial resolution, lack of spatial linearity.

Tests that are not performed because of lack of needed devices are system counting speed, system senility, registration of own spatial in many windows and blind age leaks.

In the weekly test of uniformity without collimator we noticed that we had problems because from calculations we saw that CFOV was 5.72% and it should be less than 5%. According to this result the test must be repeated by increasing the number of counts.

In the annual test of uniformity with collimator, we saw that from calculations CFOV was 1.3% and it was within the proper parameters.

In the test of own resolution energy, the average value of GJL calculated automatically from the software was 9.25% and it was within the proper parameters less than 10%.

Results that are taken after each test showed that we have an energy window well squared within the given parameter.

The importance of quality control in ensuring the normal working of the equipment, within the allowed parameters, provides the appropriate image quality, which deals directly with the accuracy of diagnosis as well as radiation protection of patients and staff.

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PRELIMINARY INVESTIGATIONS ON TERNARY AND/OR QUATERNARY CHALCOGENIDE-HALIDES WITH THE ELEMENTS OF THE IIND B AND IVTH A GROUPS

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ABSTRACT

The results of preliminary investigations regarding some solid state reactions between the elements and/or binary compound containing elements of the IInd B / IVth A and VIth + VIIth groups are reported. Within the selected stoichiometric combinations and reaction conditions, four of them revealed some peculiarities. In each case, the reactions aiming the syntheses of Tin-selenide-dichloride/dibromide resulted in air sensitive products. Low-crystallinity/amorphous character of the products affected by decomposition/hydrolysis makes quite difficult the phase identification, represented mainly by the starting elements and binary compounds. Within the trial of unsuccessful reactions, two new phases are observable from the reactions intending the synthesis $PbSeI_2$ and $PbTeI_2$ along with allotropic forms of identifiable binary compounds.
Keywords: Solid state reactions, new phases, tin-selenide-dichloride/dibromide, lead-selenide/telluride diiodide, air sensitive, amorphous character

1. INTRODUCTION

The determination of the mixed valence character of indium and the obtained structures are of great interest for a series of substitution of indium species mainly by alkaline metals (Na, K, Rb, Cs), thalium and rarely with *d*-elements (e.g. Cr). These substitutions, along with the previous substitution of indium in its normal valence compounds enlarged further the spectrum of ternary compounds.

The structural elements (building units) of these compounds intrigued many solid state researchers. Their combination possibilities are of great interest. Many pioneer researches including this concept enriched the diversity of the mixed valence compounds, with the compounds MIn_5S_6 {M = Tl, K} (Deiseroth

and Walther, 1995; Deiseroth and Reiner, 1998) and MIn_7Ch_9 {M = Rb, Cs; Ch = S, Se} (Reiner *et al*., 2002; Reiner and Deiseroth, 1999) which interlace the existing and new structural units. In this course of investigations on the mixed valence compounds, Paashaus and Kniep (1990) including other elements of the third A- group and *halogens*, revealed another group of compounds with interesting structure M_3Te_3X, {M = Al, Ga, In; X = Cl, Br, I} which surprisingly were carrying the above concept.

Pursuing this trend shown by indium and/or other third group elements in combination with chalcogenides and halides, the present paper aims at investigating the conditions for the syntheses of ternary and/or quaternary chalcogenide-halides with the elements of the IInd B and IVth A group. In this context, information about the combining possibilities of building units with the aim of new structures is here reported.

A quick review of the literature reveals the total absence of chalcogenide halides of cadmium, unlike tin and lead which are represented by some ternary chalcogenide halides as reported in table 1.

Table 1: Ternary chalcogenide halides of Cd, Sn and Pb

	S + Cl	**S + Br**	**S + I**	**Se + Cl**	**Se + Br**	**Se +I**	**Te + Cl**	**Te +Br**	**Te +I**
Cd	-	-	-	-	-	-	-	-	-
Sn	-	$Sn_7S_2Br_{10}$ [1]	Sn_2SI_2[2] $SnS_{16}I_4$[3] Sn_4SI_6 [4]						
Pb	-	$Pb_7S_2Br_{10}$[5]	$Pb_5S_2I_6$[5]		Pb_4SeBr_6[5]		$PbTeCl_2$[6]		

[1] Valle *et al.*, (1984); [2] Fenner, (1976); [3] Hawes, (1962); [4] Fenner, (1978); [5] Krebs, B. (1973); [6] Genkin *et* al., (1985)

The latter mentioned elements build mix crystals with chalcogenides as in $PbTe_3$ $(CL,S)_2$ Genkin *et al*., (1985) and $SnSe_2S_{14}I_4$ (Laitinen *et. al*., 1980) or quaternary compounds with antimony $Sn_2SbSe_2I_3$, $Sn_3SbSe_2I_5$ (Ibanez *et al*., 1984).

2. EXPERIMENTAL

2.1 PREPARATION PROCEDURE

The present investigation involved several elements and binary starting compounds for the syntheses. All of them were supplied by the chemical company Sigma-Aldrich. Their consistence and the purity are listed in table 2.

Table 2: The constitution, origin and purity of the used chemicals

Element / Compound	Consistence	Producer	Purity
Cd (Cadmium)	granules	Sigma - Aldrich	purum p.a., for metal reduction, 99.99%
I_2 (Iodine)	pieces	Sigma - Aldrich	99.999% trace metals basis
Pb (Lead)	shots <2 mm	Sigma - Aldrich	99.9% trace metals basis
S (Sulfur)	pieces	Sigma - Aldrich	purum p.a., ≥99.5%
Se (Selenium)	pellets < 4 mm	Sigma - Aldrich	≥99.99% trace metals basis
Sn (Tin)	granules 0.425-2.0 mm particle size	Sigma - Aldrich	≥99.5%
Te (Tellurium)	pieces	Sigma - Aldrich	99.999% trace metals basis
$CdCl_2$ (Cadmium chloride)	powder	Sigma - Aldrich	anhydrous, puriss. p.a., ≥99.0%
$PbBr_2$ (Lead(II) bromide)	powder	Sigma - Aldrich	99.999% trace metals basis
$PbCl_2$ (Lead(II) chloride)	powder	Sigma - Aldrich	99.999% trace metals basis
$SnBr_2$ (Tin(II) bromide)	powder	Sigma - Aldrich	-
$SnCl_2$ (Tin(II) chloride)	powder	Sigma - Aldrich	reagent grade, 98%

Initially for the preparation of the ternary and quaternary compounds, elements and binary educts in stoichiometric proportions were weighed in each case respecting the stoichiometry. Generally 1g of starting compounds mixture was transferred into preheated and evacuated quartz ampoule. The ampoules were evacuated and sealed in H_2-O_2 flame. The obtained sealed ampoule in each case was weighted and annealed over variable time periods at different temperatures. In most cases, the heating and cooling process succeeded according to temperature programs with variable heating. Here, cooling rates were used. Afterwards the ampoules were opened in air and their content was mortared and analysed by X-ray powder diffractometery. Detailed specialised measurements in random sample micro-volumes were performed by means of a Bruker-AXS D8 Discover XRD system.

2.2 CHARACTERISATION

2.2. 1 X-RAY DIFFRACTION OF POWDERED SAMPLES

X-ray powder diffraction was performed with a Huber G670 Guinier camera with a fixed imaging plate and an integrated read-out system [Cu-$K\alpha_1$ radiation, Ge (111) monochromator, λ= 1.54051 Å]. Representative parts of the samples

were crushed and fixed between Mylar foils using vacuum grease. The X-Ray data software package VISUAL X^{POW} and WIN X^{POW} delivered from the "STOE" company were used for the indexation of the reflections and their refinement.

2.2.2 X-RAY DIFFRACTION OF SELECTED AREAS IN BULK SAMPLES

The data were collected on a Bruker-AXS D8 Discover XRD system (Bruker AXS GmbH, Germany) equipped with a general area detector diffraction system (GADDS), a Gobel mirror, a 0.5mm pinhole collimator, and a Bruker-Vantec-500 area detector was used. The X-ray generated from a sealed Cu tube (40kV and 40mA) is monochromated by a graphite crystal and collimated by a 0.5mm MONOCAP (λ Cu-Kα = 1.54178 Å). The samples were scanned using the following parameters: omega = 4°, detector swing angle = 18°, sample to detector distance = 20cm and exposure time = 180s. Bruker-AXS GADDS system software integrated area from 2Ÿ = 10 to 80°.

3. DISCUSSIONS

Most of the investigated compositions between the elements of the II^{nd} B / IV^{th} A and VI^{th} + VII^{th} groups (Table 3) didn't show new phases within the investigated temperature/temperature programs. Anyway, within these trials, the four stoichiometric combinations that revealed some peculiarities which require further attention are No. 8, 9, 13 and 14. The stoichiometric compositions 8 and 9 which aimed the syntheses of Tin-selenide-dichloride/dibromide resulted to be air (moisture) sensitive. Upon their contact to air (right after opening the ampoule) vigorous reaction were observed in both cases, revealing their highly hygroscopic character.

Table 3: Educts, expected products, conditions and the obtained products. On the right column are listed the PDA No. of the obtained elements and/or compounds.

No.	Educts	Expected product	Conditions	Products	PDA No.
1	Cd, S, I_2	Cd_2SI_2	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 60$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	CdS, CdI_2	CdS 00-001-0780 CdS 00-006-0314 CdI_2 00-033-0239
2	Cd, Se, I_2	Cd_2SeI_2	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 55$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	CdSe, CdI_2	CdSe 00-008-0459 CdSe 00-077-2307 CdI_2 00-033-0239 CdI_2 00-071-0798 CdI_2 00-085-1112
3	Cd, Te, I_2	Cd_2TeI_2	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 55$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	CdTe, CdI_2	CdTe 00-010-0207 CdTe 00-015-0770 CdI_2 00-033-0239 CdI_2 00-085-1112
4	$CdCl_2$, Cd, Te	Cd_2TeCl_2	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 60$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	$CdCl_2$, CdTe	$CdCl_2$ 00-009-0401 $CdCl_2$ 00-085-0883 $CdCl_2$ 00-089-1568 CdTe 00-015-0770
5	Sn, S, I_2	$SnSI_2$	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 55$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	SnI_4, SnS_2	SnI_4 00-006-0232 SnI_4 00-077-0139 SnS_2 00-022-0951 SnS_2 00-023-0677
6	Sn, Se, I_2	$SnSeI_2$	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 55$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	SnI_4, $SnSe_2$	SnI_4 00-006-0232 SnI_4 00-006-0234 SnI_4 00-077-0139 $SnSe_2$ 00-040-1465

7	Sn, Te, I_2	$SnTeI_2$	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 55$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	SnI_2, Te	SnI_2 00-028-1391 SnI_2 00-070-1492 Te 00-078-2312 Te 00-079-0736
8	$SnCl_2$, Se	$SnSeCl_2$	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 55$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	(air sensitive) HCl(g) + $SnSe_2$, $SnCl_2$,	$SnSe_2$ 00-023-0602 $SnSe_2$ 00-040-1465 $SnCl_2$ 00-072-0137
9	$SnBr_2$, Se	$SnSeBr_2$	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 55$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	(air sensitive) (brownish liquid) + $SnSe_2$	$SnSe_2$ 00-023-0602 $SnSe_2$ 00-040-1465
10	$SnCl_2$, Te	$SnTeCl_2$	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 55$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	Unreacted educts $SnCl_2$, Te	-
11	$SnBr_2$, Te	$SnTeBr_2$	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 55$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	$SnBr_2$, Te	$SnBr_2$ 00-028-1383 Te 00-036-1452 Te 00-078-2312 Te 00-086-2269
12	Pb, S, I_2	$PbSI_2$	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 55$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	layered compound + partially non reacted S	S_8 00-078-1888 $Pb_{1.1785}I_{3.570}$ 00-080-1001
13	Pb, Se, I_2	$PbSeI_2$	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 55$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	layered compound PbSe, Se	New + PbSe + Se PbSe 00-077-0245 Se 00-086-2246
14	Pb, Te, I_2	$PbTeI_2$	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 55$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	(layered compound)	New + Te Te 00-004-0554 Te 00-036-1452
15	$PbCl_2$, Se	$PbSeCl_2$	$RT \xrightarrow{10^{\circ}/h} 250°C(5d) \xrightarrow{10^{\circ}/h} 60$ $0°C(5d) \xrightarrow{20^{\circ}/h} RT$	$PbCl_2$	$PbCl_2$ 00-005-0416 $PbCl_2$ 00-026-1150 $PbCl_2$ 00-072-0440

16	$CdCl_2$, Cd, Se	Cd_2SeCl_2	RT $\xrightarrow{10^{\circ}/h}$ 250°C(5d) $\xrightarrow{10^{\circ}/h}$ 58 0°C(5d) $\xrightarrow{20^{\circ}/h}$ RT	CdSe, $CdCl_2$	CdSe 00-008-0459 CdSe 00-019-0191 CdSe 00-077-2307 $CdCl_2$ 00-009-0401 $CdCl_2$ 00-085-0883
17	$CdCl_2$, Sn, Se	$CdSnSeCl_2$	RT $\xrightarrow{10^{\circ}/h}$ 250°C(5d) $\xrightarrow{10^{\circ}/h}$ 58 0°C(5d) $\xrightarrow{20^{\circ}/h}$ RT	CdSe,$CdCl_2$, SnSe, $SnCl_2$	CdSe 00-077-2307 $CdCl_2$ 00-085-0883 $CdCl_2$ 00-089-1568 SnSe 00-048-1224 SnSe 00-089-0232 $SnCl_2$ 00-072-0137
18	$CdCl_2$, Sn, Te	$CdSnTeCl_2$	RT $\xrightarrow{10^{\circ}/h}$ 250°C(5d) $\xrightarrow{10^{\circ}/h}$ 58 0°C(5d) $\xrightarrow{20^{\circ}/h}$ RT	SnTe, $CdCl_2$	SnTe 00-008-0487 SnTe 00-025-0465 SnTe 00-046-1210 $CdCl_2$ 00-009-0401 $CdCl_2$ 00-085-0883
19	$CdCl_2$, Pb, Se	$CdPbSeCl_2$	RT $\xrightarrow{10^{\circ}/h}$ 250°C(5d) $\xrightarrow{10^{\circ}/h}$ 58 0°C(5d) $\xrightarrow{20^{\circ}/h}$ RT	$PbCl_2$, CdSe	$PbCl_2$ 00-005-0416 $PbCl_2$ 00-026-1150 $PbCl_2$ 00-072-0440 CdSe 00-008-0459
20	$CdCl_2$, Cd, Te	Cd_2TeCl_2	RT → 550°C (10 days) → RT	$CdCl_2$, CdTe	$CdCl_2$ 00-009-0401 $CdCl_2$ 00-085-0883 CdTe 00-015-0770
21	$PbCl_2$, Te	$PbTeCl_2$	RT → 550°C (10 days) → RT	$PbCl_2$	$PbCl_2$ 00-005-0416 $PbCl_2$ 00-026-1150 $PbCl_2$ 00-072-0440

In case of the stoichiometric composition No.8 (Table 3), fuming HCl was formed along with a remaining dark grey solid, which according to the powder-XRD analysis resulted to be different allotropic forms of $SnSe_2$ (Tin diselenide) (Fig. 1).

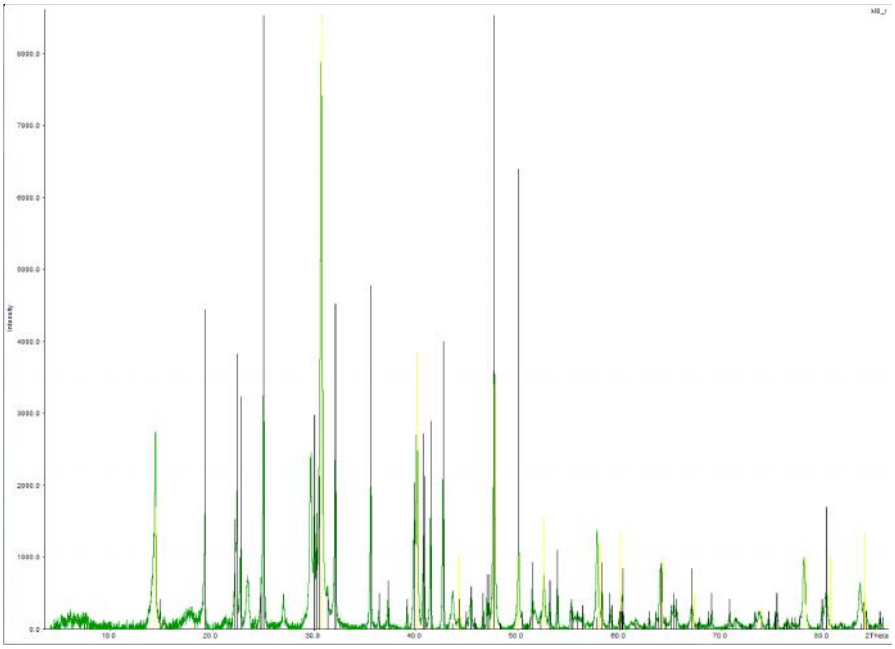

Fig. 1: Diffraction pattern of the sample obtained from the stoichiometric composition No. 8. Its reflections were indexed according to different allotropic forms of $SnSe_2$ (showed by different colours of fitting lines).

In case of the stoichiometric composition No. 9 (Table 3), a brown liquid was formed along with a brownish-gray crystalline solid, which according to the powder-XRD analysis revealed a diffraction pattern with low crystallinity resulting to be mainly $SnSe_2$ (Tin diselenide) (Fig. 2). Unlike the diffraction pattern of sample No. 8, sample No. 9 showed a higher amorphous character which made quite difficult the phase identifications. In spite of it, the solid sample was investigated further with Bruker-AXS D8 Discover XRD system, exhibiting a diffraction pattern with reflections of $SnSe_2$, along with further reflections which could be indexed to elemental Sn, Se and $SnBr_4$ (Fig. 3).

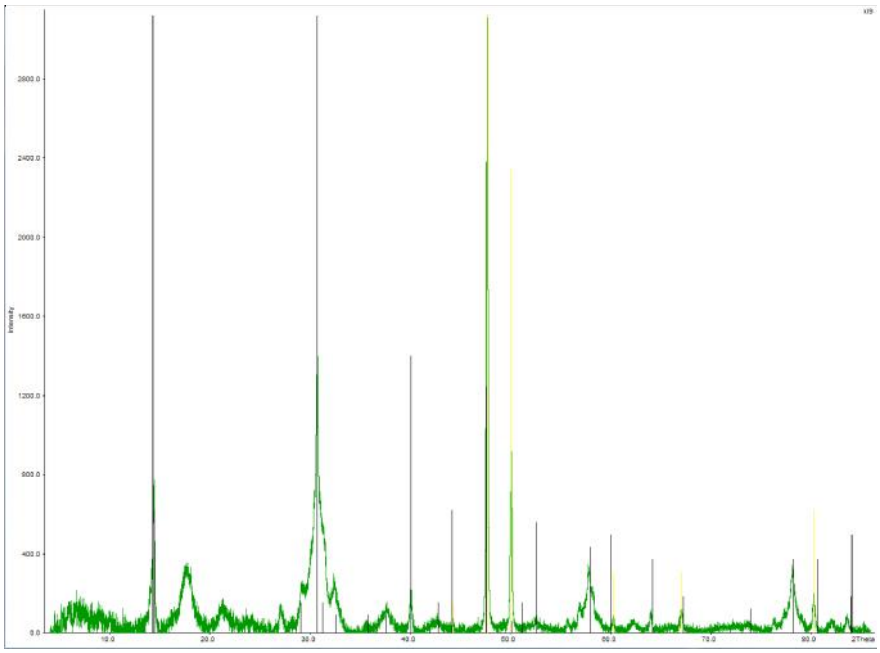

Fig. 2: Diffraction pattern of the sample obtained from the stoichiometric composition No. 9. Despite of the low crystallinity, most of its reflections were indexed according to two different allotropic forms of $SnSe_2$ (indicated by different colours of fitting lines).

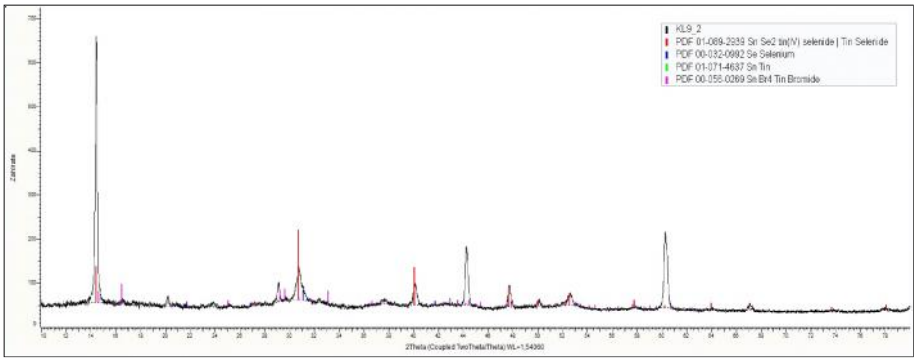

Fig. 3: Diffraction pattern of sample No. 9 recorded with a Bruker-AXS D8 Discover XRD system, showing the presence of reflections belonging to $SnSe_2$, Se, Sn and $SnBr_4$.

Since the starting compounds $SnCl_2$ and $SnBr_2$ were of reagent grade, their adsorbed and crystal water content might have a definite role in the supposed syntheses. Despite the high reaction temperature, the presence of elements found in the product leads to the conclusion of the occurrence of dissociation and/or hydrolysis. Therefore, according to the obtained data from the diffraction

patterns, a generalised mechanism of the dissociation of $SnSeCl_2$ and $SnSeBr_2$ is proposed:

$$\mathbf{SnSeX_2 \rightarrow Sn + Se + SnSe + SnX_4\ (X = Cl, Br)}$$

The attempts to synthesize $PbSeI_2$ (No. 13, Table 3) and $PbTeI_2$ (No. 14, Table 3), resulted in layered samples consisting of new phases accompanied by usual binary compounds (Fig. 4 a, b; 5 a,b)

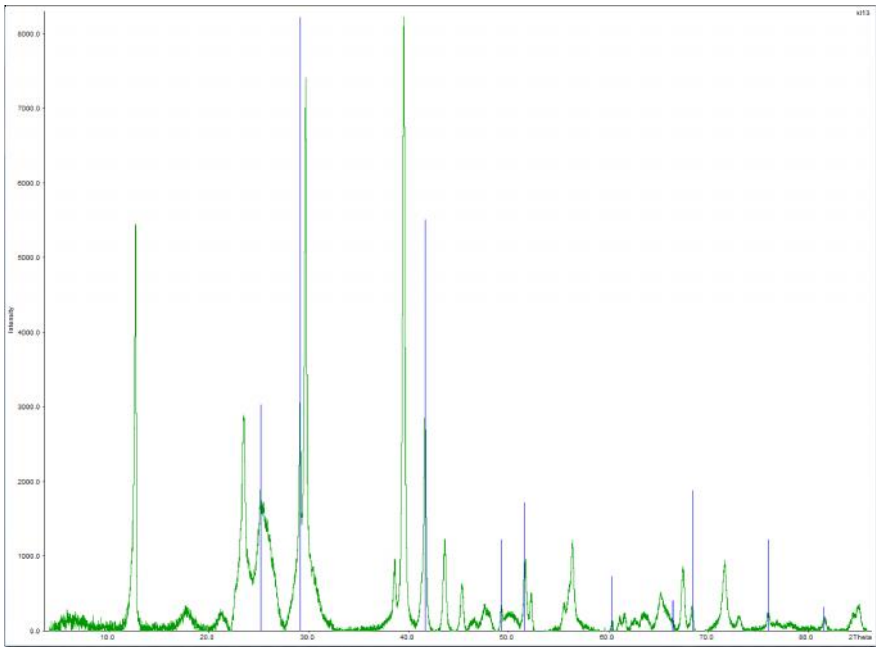

Fig. 4a: Diffraction pattern of sample No. 13, with some reflections indexed according to PDA 00-077-0245 corresponding to PbSe. Unindexed reflections are indicated by arrows.

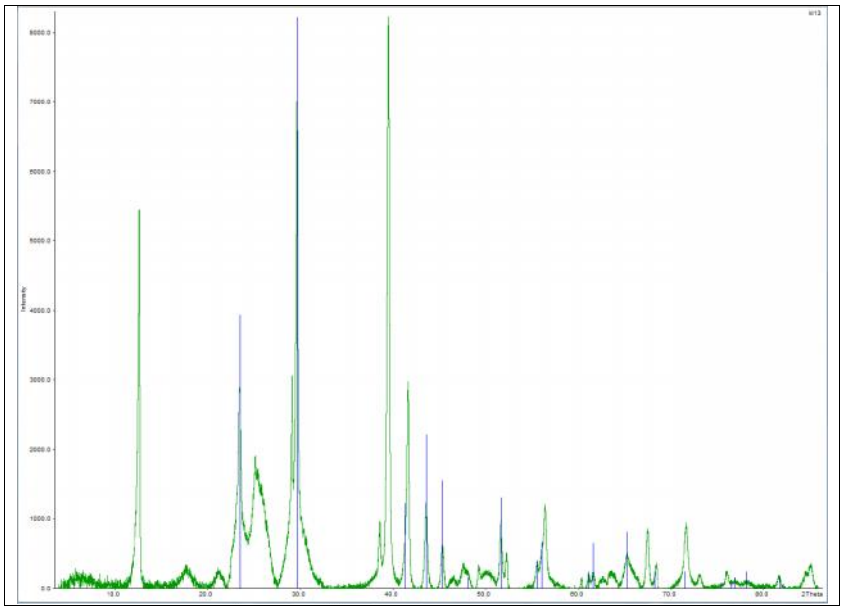

Fig. 4b: Diffraction pattern of sample No. 13, with some reflections indexed according to PDA 00-086-2246 corresponding to Se. Unindexed reflections are indicated by arrows.

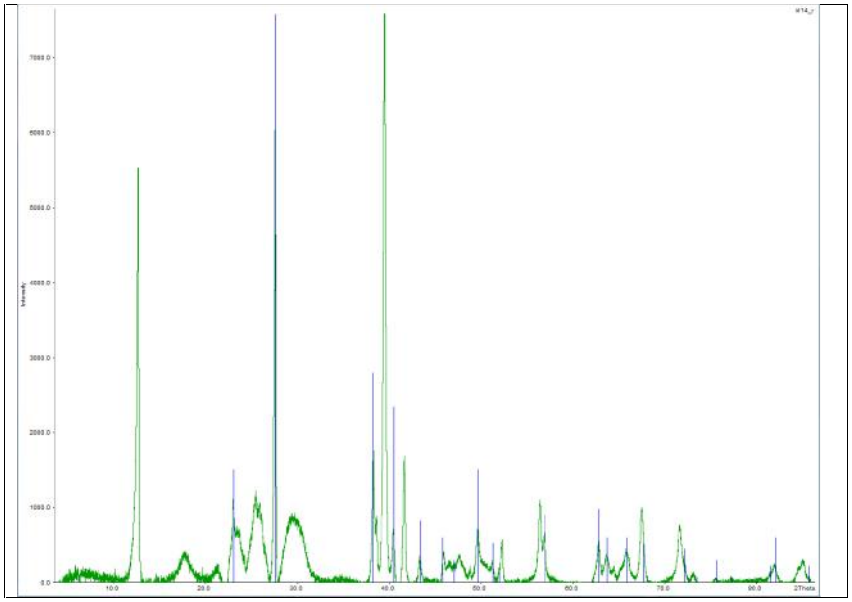

Fig. 5a: Diffraction pattern of sample No. 14, with some reflections indexed according to PDA 00-004-0554 corresponding to Te. Unindexed reflections are indicated by arrows

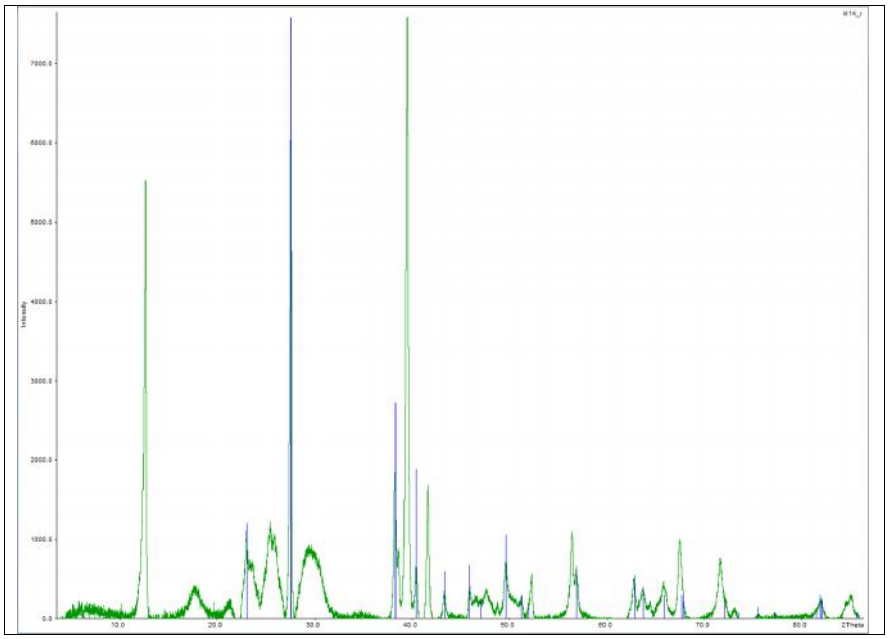

Fig. 5b: Diffraction pattern of sample No. 14, with some reflections indexed according to PDA 00-036-1452 corresponding to Te. Unindexed reflections are indicated by arrows

A closer observation to the diffraction patterns of fig. 4a,b; 5a,b reveals the presence of some reflections which cannot be indexed with the chosen patterns (pointed by arrows). Further detailed measurements performed with Bruker-AXS D8 Discover XRD system, exhibited the occurrence of reflections belonging to PbI_2 (except Se and PbSe) in case of sample No.13 (Fig. 6) and two allotropic forms of PbI_2 (except Te) in case of sample No. 14 (Fig. 7).

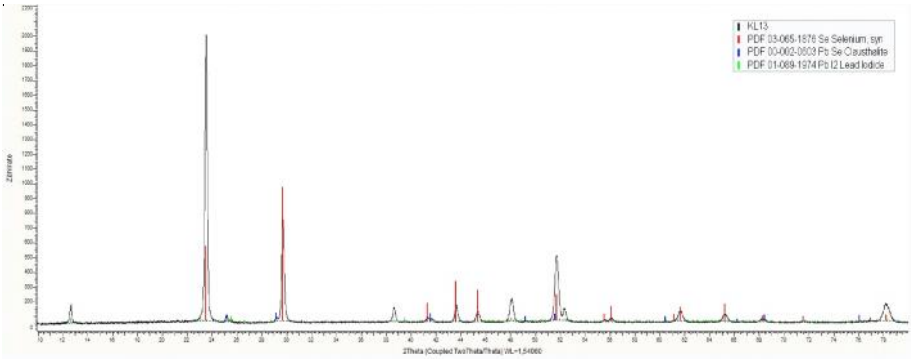

Fig. 6: diffraction pattern of sample No. 13 recorded with a Bruker-AXS D8 Discover XRD system, showing the presence of reflections belonging to PbSe, Se and PbI_2.

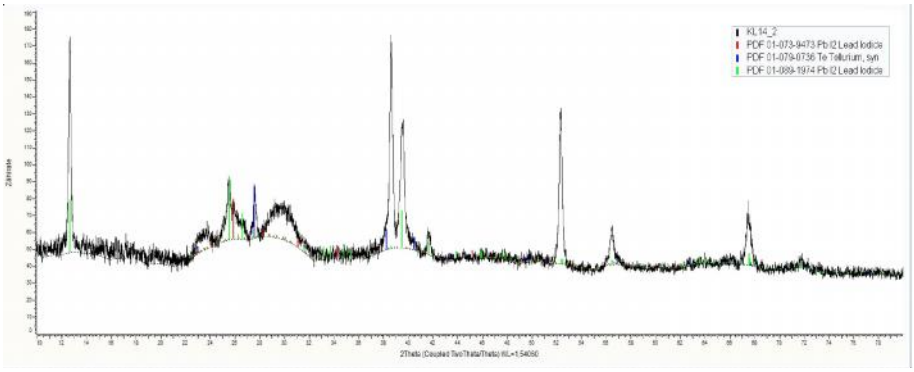

Fig. 7: diffraction pattern of sample No. 14 recorded with a Bruker-AXS D8 Discover XRD system, showing the presence of reflections belonging to Te and two allotropic forms of PbI_2.

4. CONCLUSIONS

The majority of the investigated compositions (Table 3) between the elements of the IInd B / IVth A and VIth + VIIth groups didn't show new phases within the investigated temperature/temperature programs. Within this list of reactions, the existence of four new phases, represented by $SnSeCl_2$, $SnSeBr_2$, $PbSeI_2$ and $PbTeI_2$ could be supposed. The first two phases were hygroscopic and hydrolised/dissociated into elements and binary compounds, meanwhile, the second new phases were accompanied partially by unreacted elements and binary compounds. The later new phases exhibit similar sum formulae to Kolarite ($PbTeCl_2$) and probably similar structure to it.

5. OUTLOOK

Based on the achieved results, the future research between the elements of the IInd B / IVth A and VIth + VIIth groups can be focused on the condition optimisation for obtaining pure phases of $SnSeCl_2$, $SnSeBr_2$, $PbSeI_2$ and $PbTeI_2$. These steps rely on two parameters: i) the purity/purification of the starting compounds, which implies the case of $SnCl_2$ and $SnBr_2$, as binary halides of tin which are always accompanied by water traces and, ii) the annealing temperature/temperature program which can be primarily optimised based on DTA/DSC measurements of chosen stoichiometric compositions.

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A REVIEW OF FLAVIVIRUSES AND FLAVIVIRUS VACCINES

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ABSTRACT

Flavivirus is a genus of viruses in the family *flaviviridae* that include the West Nile virus, dengue virus, tick-borne encephalitis virus, yellow fever virus that cause encephalitis. Some of the vaccines against flavivirus are used to protect the population living in endemic regions or those who travel in such regions and some others are in different phases of development. Aiming to provide an accurate information about the risks of flavivirus infection, the present paper reviewes on effective human vaccines in use for the prophylaxis of yellow fever (YF), dengue, Japanese encephalitis (JE), West Nile (WN).
***Keywords*:** infection, virus, vaccine, fever

1. INTRODUCTION

General information about flavivirus vaccination

A vaccine is a biological preparation that improves immunity to a particular disease. It typically contains an agent that resembles a disease-causing microorganism, and is often made from weakened or killed forms of the microbe, its toxins or one of its surface proteins. The agent stimulates the body's immune system to recognize the agent as foreign, destroy it, and "remember" it, so that the immune system can more easily recognize and destroy any of these microorganisms that it later encounters (WHO 2014 last update).

Yellow fever virus (YFV) is found in tropical and subtropical areas in South America and Africa. The virus is transmitted to humans by the bite of mosquito named *Aedes aegypti*. Other mosquitoes such as tiger mosquito can serve as a vector. Illness ranges in severity from a self-limited febrile illness to severe liver disease with bleeding and is diagnosed based on symptoms, physical findings,

laboratory testing, and travel history, including the possibility of exposure to infected mosquitoes. There is no specific treatment for yellow fever; care is based on symptoms. Steps to prevent yellow fever virus infection include using insect repellent, wearing protective clothing, and getting vaccinated (CDC 2011).

With more than one-third of the world's population living in areas at risk for infection, dengue virus is a leading cause of illness and death in the tropics and subtropics. As many as 400 million people are infected yearly. Dengue is caused by any one of four related viruses transmitted by mosquitoes. There are not yet any vaccines to prevent infection with dengue virus and the most effective protective measures are those that avoid mosquito bites. When infected, early recognition and prompt supportive treatment is substantially lower the risk of medical complications and death (CDC 2014).

Dengue has emerged as a worldwide problem only in the 1950s. Although dengue rarely occurs in the continental United States, it is endemic in Puerto Rico and in many popular tourist destinations in Latin America, Southeast Asia and the Pacific islands (CDC 2014).

Japanese encephalitis (JE) virus is the leading cause of vaccine-preventable encephalitis in Asia and the western Pacific. For most travelers to Asia, the risk of JE is very low but varies based on destination, duration of travel, season, and activities. JE virus is maintained in a cycle involving mosquitoes and vertebrate hosts, mainly pigs and wading birds. Humans can be infected when bitten by an infected mosquito. Most human infections are asymptomatic result in only mild symptoms. However, a small percentage of infected persons develop inflammation of the brain (encephalitis), with symptoms including sudden onset of headache, high fever, disorientation, coma, tremors and convulsions. About 1 in 4 cases are fatal. There is no specific treatment for JE. Patient management focuses on supportive care and management of complications. Steps to prevent JE include using personal protective measures to prevent mosquito bites and vaccination (CDC 2012).

West Nile Virus (WNV) which is an arbovirus (arthropod- borne viruses) (Gould and Solomon, 2008) is transmitted to humans primarily through the bites of infected mosquitoes and ticks. West Nile Virus (WNV) can cause neurological disease and death in people. WNV is commonly found in Africa, Europe, the Middle East, North America and West Asia.

Dengue vaccines against dengue virus

Dengue infection can appear with or without symptoms (WHO 1997; Beatty *al*., 2008).

In human, the virus can cause a spectrum of illness ranging from asymptomatic infection or self-limiting influenza-like illness (dengue fever or DF) to life-threatening disease associated with vascular leakage, hemorrhage (dengue

hemorrhagic fever or DHF), potentially leading to vascular shock (dengue shock syndrome or DSS) (Andries *et al.*, 2012).

If the infection does not have any symptom (asymptomatic) the infection is mild.

The figure 1 depicts the performance of dengue infection development over time.

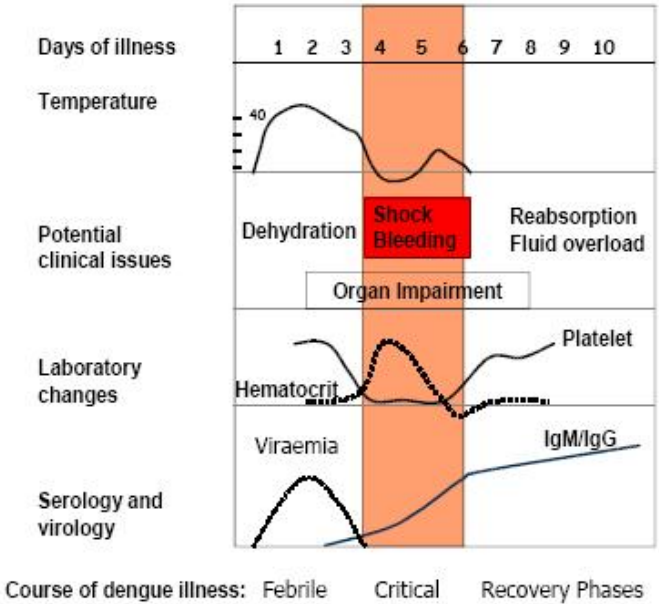

Fig. 1: The development stage of dengue infection dependence the time (Clinical Practice Guideline, 2008).

An estimated 50 million dengue infections occur annually and approximately 2.5 billion people live in over 125 dengue endemic countries. Two million cases evolve to severe Dengue Hemorrhagic Fever, and 21 000 would result in death (WHO 2009; Beatty *et al*., 2008).

Neutralization of the virus via antibodies and dengue candidate vaccines are of great impact for the prevention of dengue diseases as high level of antibody neutralization is obtainable.

The vaccine of dengue prevents symptomatic dengue, covering the spectrum from dengue fever to severe dengue cases due to serotypes 1 - 4, improve quality of life and decrease case fatality ratio (CFR).

Dengue vaccines in development are of four types: live attenuated viruses, chimeric live attenuated viruses, inactivated or sub-unit vaccines, and nucleic acid-based vaccines.

Live attenuated vaccines (LAVs) can induce durable humoral and cellular immune responses since they most closely mimic a natural infection. Several parameters are crucial for LAVs: i) the viruses must be sufficiently attenuated and viral replication reduced so that viraemia is low and symptoms of illness are minimal, ii) transmission of the viruses by mosquitoes is reduced or eliminated, iii) the viruses should replicate well in cell culture and be sufficiently immunogenic to provide long-lasting immunity in humans, so that low doses can be used, iv) a balanced immune response to all four dengue viruses must be elicited and, v) the genetic basis for attenuation must be known and must be stable (Whitehead *et al.*, 2011).

The vaccine against yellow fever

Yellow fever is a vector borne disease resulting from the transmission of yellow fever virus (YFV) to a human from the bite of an infected mosquito. It is endemic to sub-Saharan Africa and tropical South America and is estimated to cause 200,000 cases of clinical disease and 30,000 deaths annually. Infection in humans is capable of producing hemorrhagic fever and is fatal in 20%–50% of persons with severe disease. Because no treatment exists for YF disease, prevention is critical to lower disease risk and mortality (CDC 2002).

A traveler's risk for acquiring YFV is determined by multiple factors, including immunization status, location of travel, season, duration of exposure, occupational and recreational activities while traveling, and local rate of virus transmission at the time of travel. Consequently, the Center for Disease Control and Prevention (2014) recommends vaccination prior to traveling to countries in which YF is endemic.

Yellow fever virus (YFV) occurs in the following transmission cycles: i) the jungle/sylvatic cycle where the virus is transmitted between susceptible monkeys, and possibly other vertebrates, by tree-hole breeding mosquitoes. Jungle yellow fever (YF) cases occur when these infected vectors feed on susceptible humans and, ii) the urban cycle where YFV is transmitted to humans by *Aedes aegypti* mosquito (Monath 1989).

Picture 2 depicts the transmission cycle of yellow fever.

Yellow fever virus has genetic diversity and geographical distribution (Barrett and Higgs 2007).

West-African yellow fever virus has greater population, less variety, slow evolution and constant growth, typical of the West African Countries.

The yellow fever virus causes viscerotropism infection, temporary viraemia, impairment in liver, spleen, kidney and heart and bleeding. In nature, the infection occurs in primates and non-human beings. Molecular mechanisms of the type of infection are incomprehensible.

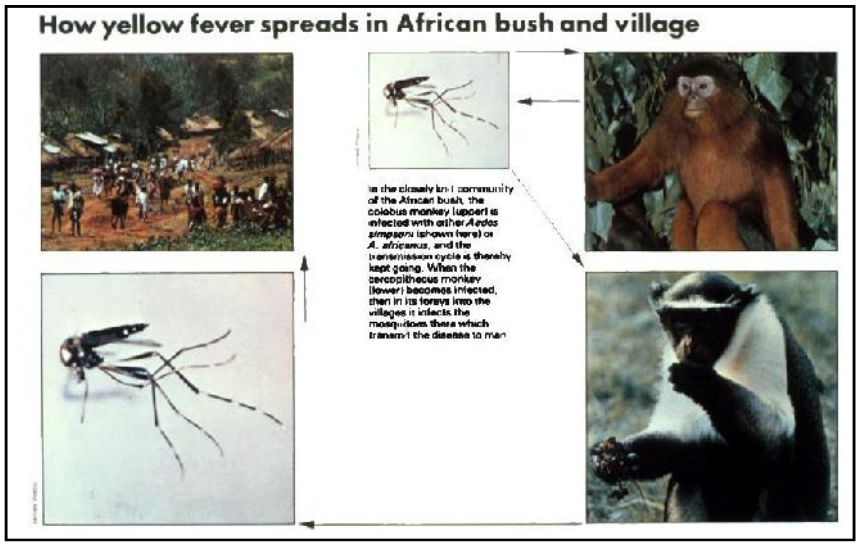

Fig. 2 Transmission cycle of yellow fever (Staples E, et al., 2010).

Neurotropism infection infects the functional part of the brain and cause encephalitis. In nature, the infection occurs in rodent of tangible and "outdoor". Wild-type viruses cannot cause neurotrophic disease (YEL-AND) (Mc Arthur *et al*., 2005).

Vaccine against West Nile virus

Although there is still no human West Nile Virus (WNV) vaccine approved today, several vaccine candidates are in development A WNV vaccine needs to protect against all WNV genotypes, particularly after the emergence of the neuroinvasive strains. The WNV vaccine for horses is approved (Brandler and Tangy 2013).

The vaccines against Japanese encephalitis

Japanese encephalitis virus (JEV) is serologically related to St. Louis encephalitis virus. An estimated three billion people are at risk and the annual incidence of the disease is 30,000-50,000 cases. The annual number of human deaths is 10,000–15,000. **JE is a vaccine-preventable disease with numerous options now available for active immunization.** Originally, the substrates for inactivated vaccines were either infected mouse brains or primary hamster kidney cells (China) (Halstead and Thomas 2010).

The types of Japanese encephalitis vaccines are: i) inactivated, mouse- brain JE, ii) Inactivated vero cell, iii) live attenuated PHK (primary hamster kidney) and, iv) live attenuated chimera, vero cell.

The vaccines against flavivirus

The development of YFV 17D live-attenuated vaccine was a landmark in the history of viral vaccines, and in 1951 Max Theiler was awarded the Nobel Prize in medicine for his achievements in attenuating the wild-type virus by serial passaging in mouse and chicken tissue (Plotkin *et al.*, 2008).

Since its development in 1937, more than 500 million people have been vaccinated and 98% of vaccines being fully protected for at least 10 years. The evolution of flavivirus vaccines has gone through three generations:

First generation

Raw suspension from 1930 to 1940 JE (Japanese Encephalitis)

Yellow fever vaccines live attenuated, developed in 1937, more than 500 million people have been vaccinated and over 98% of vaccines are believed to be protected for at least 10 years (Barrett and Teuwen 2009).

Originally, the substrates for inactivated vaccines were either infected mouse brains or primary hamster kidney cells (China) and vaccine efficacies of 76–95% were reported (Halstead and Thomas 2010).

Second generation: Purified virus 1950- 1970.
Used tissue or primary cells, wild-type- virus

Primary hamster kidney JE (China)	Chick embryo JE (USA)

The cell culture- derived vaccines are manufactured and widely used in China.The SA 14-14-2 vaccine strain was obtained from its wild type SA 14 parent by serial passages in cell cultures (primary hamster kidney cells-PHK cells) and in animals (mice, hamsters) with successive plaque purifications (in primary chick embryo cells).

Brain of mouse, purified JE (Japan)

The mouse brain derived, purified and inactivated vaccine, is based on either the Nakayama or Beijing strains of the japanese encephalitis.

Third generation: purified (adjuvanted) 1980

Chick embryo cell (alum) Tick Born Encephalitis Austria

Cell line, attenuated virus 1990- 2010

Vero cell JE (Japan, China) JE SA14-14-2 Alum (USA, Austria) YF alum (USA) Dengue (USA)

New dengue vaccines are in advanced clinical development, vaccines against West Nile Virus are under clinical trial. Especially third generation vaccine technology is advancing and showing promise.

Third generation vaccine technology is advancing and shows the promise for increasing of the effectiveness and safety of them.

The clinical trials are performing for human tetravalent candidate dengue vaccines and dengue contain chimera of all 4 dengue serotypes (Coller and Clements 2011).

The developmental perspective of vaccines against flavivirus (Koraka *et al.*, 2010)

Table 1 provides information about the vaccines against flavivirus which are approved for using and others that are developing.

Table 1. The vaccines against flavivirus used and under developing

Virus	Existing vaccines	Target Species
Yellow Fever (YF)	yes	human
Dengue (DEN)	yes	human, horse, pig
Japanese Encephalitis(JE)	yes	human
Tick- Borne Encephalitis (TBE)	yes	human
West Nile (WN)	yes (veterinary)	human, horse, birds (e.g. goose)
Kyasanur Forest disease	yes	human
Murray Valley Encephalitis	no	human
St. Louis encephalitis	no	human
Rocio	defunct	human
Loupingill	defunct	ship, human

2. CONCLUSION

Several human-pathogenic flaviviruses such as yellow fever, dengue, Japanese encephalitis, West Nile and tick-borne encephalitis viruses have a significant public health impact in different parts of the world and the potential of emerging in previously non-endemic regions. Vaccination is highly recommended for the population living in the endemic countries and those who travel in such countries.

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PHYSICOCHEMICAL QUALITY OF RAW MILK FROM DAIRY FACTORIES IN 5 ALBANIAN REGIONS

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ABSTRACT

The present investigation aims at evaluating the physicochemical quality of raw milk in 5 different regions of Albania. 79 raw milk samples were collected twice a day (in the morning and at evening) from Milk Processing Plants and transported to the factories in October 2013. Various physiochemical properties of milk were analyzed and compared with Albanian standard. The results showed fat 3.85±0.96 (%), protein 28.6±2.1 (g/l), solid-not-fat (SNF) 8.77±0.88, (%) density 1.0298 ± 0.002 (kg/l) and acidity 17.37±3.02 °T. The data were statistically analyzed and the results did not report any significant difference between the present results and Albanian standard at the level of $p<0.001$ which implies good quality raw milk. In addition, no adulteration of milk was found. Consequently, the raw cow milk entering in factories have good physicochemical qualities.

Key words: raw milk, fat, protein, SNF, density, acidity, milk quality.

1. INTRODUCTION

The quality of raw milk, in conformity with consumers requirements, determined by chemical composition, physicochemical properties, microbiological quality, sensory properties, technological suitability and nutritive values. Milk quality and safety are important consumer requirement. Consequently, assuring high quality and desirable physicochemical properties of raw milk destined for processing is challenging as they depend on many factors like breed, pasture etc. Fresh milk deteriorates easily becoming unsuitable for processing and human

consumption (FAO 2001). The major components of cow milk are water (87.4%), milk solids (12.60%), solids-not-fat (8.5.0%), fat (3.60%), protein (3.40%), milk sugar or lactose (4.90%) and ash or minerals (0.70%) (Albanian Regulation 2011). Currently, the process of milk collection from farmers is time-consuming, costly and prone to differences. The quality of raw milk is based on detailed and accurate monitoring of its physicochemical properties. The higher the quality of raw milk and the better the physiochemical properties are, the greater the benefit for both milk industry and consumer is.

Physicochemical parameters of cow's milk depend on SNF, TS, acidity and total bacterial count (TAC) along with protein and fat content. World Health Organization and (Grimley *et al*., 2009) emphasized that the content of milk should be: 3.6% fat, 28 g/l proteins, 7.71% SNF and LR 1.030. The pH 6.6 ensures the milk freshness at boiling point 100^{o}C -117^{o}C (Webb *et al*., 1974; Hassan 2005; Imran *et al*., 2008; Shojaei and Yadollahi 2008).

In Albania, milk is produced traditionally by village sedentary system (traditional ranch), the semi-modern system using crossbred cows with traditional treatment and the modern system. In the present paper, samples were collected from milk submitted to the aforementioned processes. Throughout the investigation period different physicochemical characteristics were reported. Fluctuation in physicochemical composition influences the milk processing (Albanian Regulation 2011).

In the present paper the physicochemical parameters are investigated to determine the condition of raw cow milk mostly used in dairy products. The samples were collected from the Agro Industries in Tirana, Durrës, Berat, Elbasan, Lezha regions.

2. MATERIALS AND METHODS

The samples were collected from 5 different Albanian regions in October 2013. They were weighed and evaluated with naked eyes for first quality checking. 200 ml milk sample was taken from each supplier to be analyzed in laboratory within 24 hours based on Albanian Standards (STASH 1500-87) and ISO Standards 707:1997.

Sampling

Fresh cow milk, in cans and bulk tanks, was thoroughly mixed to disperse the milk fat before collection of milk sample for physicochemical analysis. Plungers and dippers were used in sampling milk from containers. A total of 79 samples were collected and analyzed at the laboratories of National Agency of Food (NFA) in compliance with STASH 1500-1/87 and ISO 707:1997.

Physicochemical Analysis

The AOAC recommendations (2000) were followed to address the physical characteristics of various milk samples. STASH recommendations (1500/1-87) were followed to address the density (LR). In the present investigation, an aerometer calibrated for the milk in 20^{o}C was involved.

The titration method expressed in Turner grade was applied in some laboratories to measure the acidity (STASH 1500/3-87). The AOAC (2000) recommendations were followed in other laboratories for the same purpose. The method related to titration of the milk acids with sodium hydroxide in the presence of phenolphthalein as indicator.

Chemical Analysis

The Lacto Scanner was used to determine the protein content of milk. The equipment was calibrated and the measurements were based on requirements defined in the user's manual.

The Gerber method (2008) was applied for the total fat content. The milk samples placed into the butyrometer Gerber were digested with sulphuric acid at 1.82 g/cm^{3} density. The fat separation is done by the amyl alcohol. The fat percentage is read on the butyrometer escalation. SNF was calculated by the following equations: SNF = (LR/4) + (0.22XFat) +0.72 = % SNF.

Statistical Analysis

The standard deviations were also calculated to control the precision of examination and provide the possibility of comparing with the properties of fresh raw milk. MINITAB 15 was used for statistical analyses. Mean, standard deviation, minimum and maximum values were obtained by using descriptive statistics. The significant differences between means were calculated at $P< 0.05$. All field observations, analytical data, and measurements were entered into a data matrix. Descriptive statistics were applied to each data set in order to analyze and interpret the results, to explain the variations in the data. Factorial analysis of the correlation was used for the reduction and organization of the results in order to indicate important implicit features. The correlated variables were grouped together and separated from other variables with low or no correlation. MINITAB 15 software package was used for data analysis.

3. RESULTS AND DISCUSSION

Compositional properties of milk analysis results and statistical data are in the Table 1 reported.

Table 1. Descriptive statistics of the results from analyzes of physicochemical parameters

Variable	Mean	Median	Interval	StDev	Variance	CoefVar	Skewness	Kurtosis
Fat	3.81	3.69	1.76-8.91	0.96	0.921	25.2	2.97	13.6
Protein	28.4	28.7	18.1-38.1	2.887	8.34	10.2	-0.47	3.01
SNF	8.73	8.9	6.27-10.2	0.817	0.667	9.4	-0.45	-0.12
Density	1.033	1.03	1.022-1.034	0.0025	6*10-6	0.24	-0.53	0.21
Acidity	17.3	18	11-25.1	3.03	9.2	17.5	0	-0.43

The coefficient of variance for most of the studied parameters (except fat content) are very low (CV<25) indicating low variance of data. The CV value of fat content (CV =25.2) is just in the limit of low variation and moderate variation range (25 < CV < 75) by classifying this parameter in the same group with the first one. The skeweness values are < 2 and kurtoisis value < 3, indicating more or less the normal distribution of the P, SNF, D and acidity parameters. Only the fat parameter has the skeweness value >2 and kurtosis value > 3 indicating that the data set of fat content in the raw milk samples are positively skewed and are not normally distributed. The distributions of the data are plotted by using individual data plot as is shown in the figure 1. As the data of fat content are not normally distributed median value is used instead of its mean. The mean values of all the physicochemical parameters are in compliance with respective standards values of the Albanian Regulation 2011.

The table 1 reports that the mean value of fat content in all the districts is slightly higher than the standard value (Albanian Regulation 2011) (>3.6%) which shows a better condition of raw milk. In someof the factories, mainly in Tirana region, the mean value of parameters is considerably higher which might be related to feedstuff, breed etc. The protein content is an important parameter for the dairy products yield. The table 1 reports that the mean value is within permissible limits (Albanian Regulation 2011) (> 28g/l) in most of the factories except for some factories spread out in all the regions where the value is lower. The low values might be related to the alteration of raw milk by farmers. The same explanation might be given for the density and the SNF plot. The acidity values seem to be lower than standard value showing in general the good quality of raw milk in all the regions.

Correlation and multivariate analysis

For better interpretation of the data set, the correlation and cluster analysis of data set were carried out and the results of correlation analysis are reported in Table 2.

Table 2. Pearson correlation between element concentrations in the studied raw milk samples

	Fat	**P**	**SNF**	**D**
Protein	-0.128			
SNF	0.045	0.118		
Density	-0.113	0.267	**0.939**[1]	
Acidity	0.159	0.051	**0.345**[2]	**0.306**[3]

Cell Contents: Pearson correlation; P-Value: [1]<0.001, [2]<0.005, [3]<0.01

Significant positive correlations (R^2=0.939, P<0.001) were found between SNF and D parameters. Weak correlations (R^2<0.4) were found between the pairs of SNF-A and D-A parameters. Intensity of the correlation between analyzed parameters in milk sample was found significant. Table 2 reports a significant correlation (P<0.001) between the SNF and density parameters. The two important positive correlations are SNF and acidity (P<005) and density and acidity (P< 001). The strong correlation between SNF and D correlation is clearly reported showing that raw milk in all districts is in compliance with the standard values and normal values of the original raw cow milk. This correlation shows that parameters are in boundaries of so-called “normal milk” and in every region, the raw milk seems to be unadulterated, in general, by any kind of adulteration used randomly.

Factor Analysis: Fat, P, SNF, D, A

Factor Analysis of the Correlation Matrix

Rotated Factor Loadings and Communalities

Varimax Rotation

Variable Factor 1 Factor 2 Communality

Fat	0.125	**0.809**	0.67
P	0.232	-0.591	0.403
SNF	**0.939**	-0.091	0.89
D	**0.918**	-0.292	0.928
A	0.603	0.36	0.494
Variance	2.158	1.227	3.385
% Var	0.432	0.245	0.677

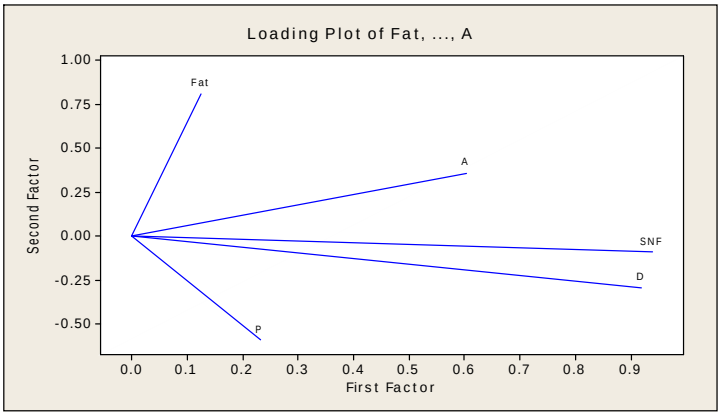

Figure 1. The diagrams of screen plot and loading plots of the raw milk parameters

Two main factors were extracted (Eigen values >1) and the minimum number of factors = 2 was selected. The results of factor analysis are in the figure 1 depicted.

The first factor explains 43.2 % of variance and high loads of SNF, density and acidity that are typical parameters of the quality of raw milk in all districts. These constituents may vary from breed and individual cow and the variability among the cows within a breed, as well as other factors such as interval between milking, stage of lactation, age, feeding regime, disease and completeness of milking. The second factor, with 24.5 % of variance also is related with acidity and may be explained with the bad management of the cold chain to transport the raw milk from farms to the factories.

4. CONCLUSIONS

Statistical analysis did not reveal any significant difference between the present results and Albanian standard at the level of $p < 0.001$ which implies good quality raw milk. There is a significant correlation between SNF and D ($P < 0,001$) which shows that raw milk in all the regions is in compliance with the standard values and normal values of the original raw cow milk. Two groups of main factors were extracted. The first factor reports that 43.2% of parameters variance depends on breed, and other factors such milking, stage of lactation, age, feeding regime etc. The second factor, with 24.5 % of variance also is related with fat. The acidity of the milk influences the fat parameter to have values instability.

In Albania, the raw cow milk entering in factory has good physicochemical

quality based on. The results here reported are very important for the governmental regulatory bodies involved in monitoring the quality of the commercial milk products in the market.

ACKNOWLEDGEMENT

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THE STABILITY OF PASTEURIZED MILK IN ALBANIA FROM 2011 TO 2013

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ABSTRACT

Pasteurization is applied to increase the shelf-life of milk and guarantee the microbiological safety via inhibition or reduction of total charge and elimination of pathogens bacteria. Practices for assessing the pasteurization status are based on heat labile of some milk components like enzymes (alkaline phosphatase, lactoperoxidase) and proteins of whey. Alkaline phosphatase is used as an indicator for the effects of pasteurization, although its thermal stability corresponds to the temperature which pathogenic microorganisms are eliminated. In the present investigation, Lacto scan was used to investigate the physicochemical indicators of quality of milk such as density, pH, percentage of proteins, fat (or triglycerides), lactose, dry matter and water added. **Added water** is the most commonly used falsification. In such a case all physicochemical indicators decreased. The analyses were carried out on the first day of opening of commercial milk and in the last day of its shelf-life, based on indications for the production and expiry date. Cultivation in standard and selective medium involving total count aerobic bacteria in PCA with skim milk; coliformes and enterobacters, also the evidence of *E. coli* in a selective Mac Coney medium was applied to investigate the microbiological indicators. Yeasts are enumerated in PDA and moulds in Capek. The samples were heated at 85ºC for 10 minutes to evaluate thermophilic microorganisms in milk. Once heated, the microorganisms were cultivated in PCA. Thermo resistant bacteria such as *Bacillus stearothermophillus* were cultivated in DTA medium. The lecithinase activity *Bacillus cereus* is an important means to address the quality of milk. In the present investigation, the quality of milk is evaluated by cultivating the bacteria in selective medium with yolk egg emulsion. The results comply with the standards defined for the total count bacteria and thermoresistant bacteria.

Keywords: milk, pasteurization, shelf-life, thermo-resistant bacteria, alkaline phosphatase.

1. INTRODUCTION

In the present paper the parameters of quality and freshness in pasteurized milk throughout its shelf-life are investigated. The samples were collected from five of the most consumed pasteurized milk in the Albanian market from March 2011 to May 2013 and evaluated in the first day of opening and in the last day of milk‘s shelf-life (expiry date). The pasteurized milk is treated at high temperature to eliminate pathogenic microorganisms making it safe for consumption and best preserve its vitamins. The present indicators of pasteurizing are investigated. Evaluation of heat treatment is possible if irreversible changes are induced in the product. The most interesting are the (bio)-chemical reactions: i) the inactivation of heat-labile components such as whey proteins or enzymes and, ii) the formation of new substances such as lactulose or the Maillard reaction products (Montilla *et al.,* 1996). Since alkaline phosphatase is stable to temperatures slightly higher than those required to destroy milk pathogens, the control of the activity of this enzyme is the most important indicator for evaluating the hygienic safety of pasteurized milk. This means that pasteurized milk must be negative for the phosphatase test (Painter *et al*., 1997). In addition the indicators of pasteurizing, physicochemical parameters such as pH (acidity), proteins, fat, dry matter, density, lactose and adulteration (by the value of added water) are evaluated using Lacto scan as it is low cost, extremely accurate equipment. It can set up and used easily. Moreover, quantitative evaluation of microorganisms in pasteurized milk during its shelf-life was carried out. Here, cultivation in standard and selective medium was used.

2. MATERIALS AND METHODS

The samples of the commercial milks from the Albanian supermarkets were collected in the first day of delivery. Once collected, the samples were transported at the laboratory where stored in fridge at low temperatures. All the used tools are sterilized in autoclave, at 121 C for 15 minutes. The Ruber test was used to investigate the activity of alkaline phosphatase. Lacto scan is in the present investigation used to measure the physicochemical parameters of the pasteurized milk (Barbano *et al.,* 2006) on the first day of opening. For the enumeration of total counts aerobic bacteria, milk and decimal dilutions are incubated on standard medium and PCA with skim milk (EU 2005 article a) at 30æ%C for 72 hours. Selective media is used to detect coliforms. Selective Mac Coney medium is used to address the enumeration of coliforms and enterobacters, and the evidence of *E. coli*. Petri dishes were incubated for 72 hours at 40^{o}C for inoculation purposes. At the end, the total number of read

colonies was counted. Thermo tolerant microorganisms were determined by preliminary treatment of the sample in 85ºC for 10 minutes. Once microorganisms were determined, milk sample and decimal dilutions were inoculated on PCA medium and Petri dishes were incubated for 72 hours at 40ºC. The same method was used for the enumeration of thermo resistant bacteria like *Bacillus stearothermophillus*. Milk sample and decimal dilutions were inoculated on selective media, DTA was incubated at 40ºC. Flat-sour colonies like *Bacillus stearothermophillus* are typically round, 2-5 mm in diameter, with an opaque centre and surrounded by a yellow zone in contrast with the purple medium. The presence of *Bacillus cereus* with lecithinase activity was determined by cultivating the bacteria on selective medium with yolk egg emulsion. Strains of *Bacillus cereus* produce enzymes, like lecithinase. Consequently, the evidence of *Bacillus cereus* could be distinguished. The assessment of yeast and mould is realized by cultivation method in PDA and Capek medium (Marshall 1993). We counted only the total count aerobic bacteria on the last day of milk's shelf-life, because the milk samples were stored at low temperatures and consequently, thermoresistant and thermotolerant microorganisms couldn't increase.

3. RESULTS AND DISCUSSIONS

Results reported that pasteurization process was carried out.

Physicochemical indicators

The Lacto scan equipment is used to measure the physicochemical indicators of milk. The results are in table 1 and 2 reported and in figure 1and 2 depicted.

Table 1. The determination of the values of chemical-physical indicators, in the first day of opening for two last years.

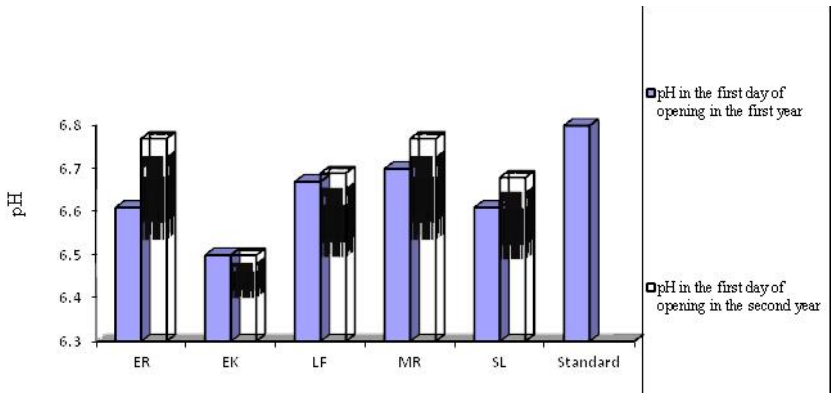

Fig. 1 The comparison of pH values, in the first day of opening (of the sample) for the two last years.

Clearly plotted in the diagram 1, the pH is within permissible limits in the first day of opening. The second year marks an increase in acidity due to the increased content of general cargo of microorganisms except of EK sample that have almost the same value of pH throughout the investigation period.

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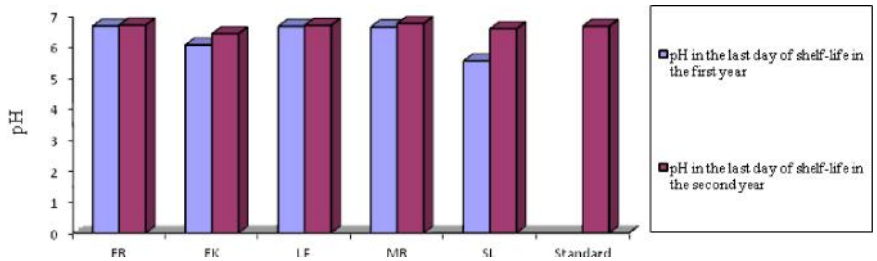

Fig.2 The comparison of pH values, in the last day of shelf-life between for the two last years

Clearly plotted in the diagram 2, the pH was close to permissible limits. The last day of the shelf-life of the second year marked an increase in acidity due to the increased content of total charge of microorganisms.

Microbiological indicators

Information about the microbiological indicators is in diagrams 1 to 8 reported.

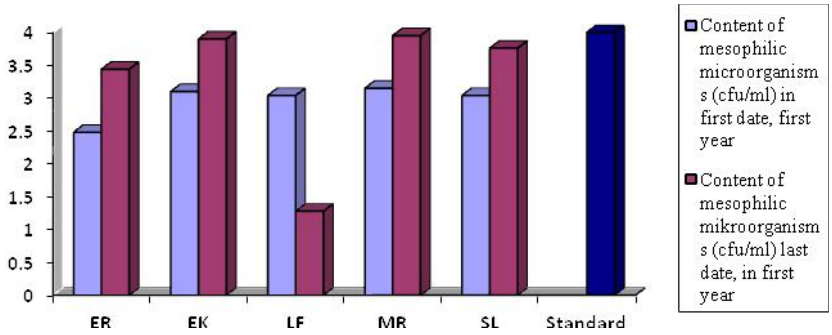

Diagram. 3. The comparison of mesophilic microorganisms content, in the first day of opening and the last day of the first year.

The diagram 3 plots the mesophilic microorganisms content higher in the last day of shelf-life than in first day (first year), due to the change of pH values. The mesophilic microorganisms content in the MR sample is near the upper limit of standard. All sample values are within permissible limits.

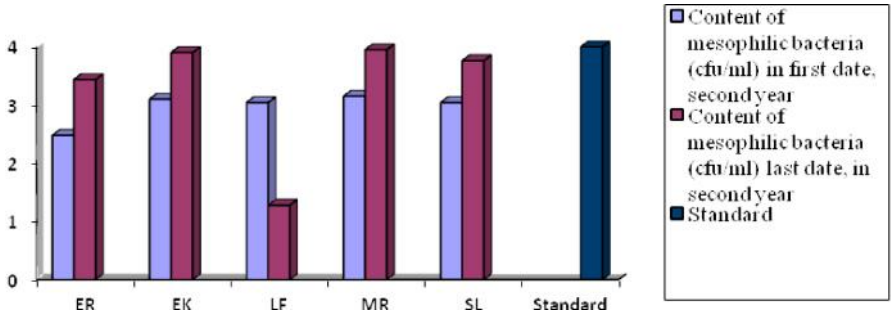

Diagram. 4 The comparison of mesophilic microorganisms content, in the first date of opening and in the last day, in second year.

In the diagram 4 it is clearly plotted that , the pH values change and the mesophilic microorganisms content is higher in last day of shelf-life(second year) than in the first. All sample values are within permissible limits.

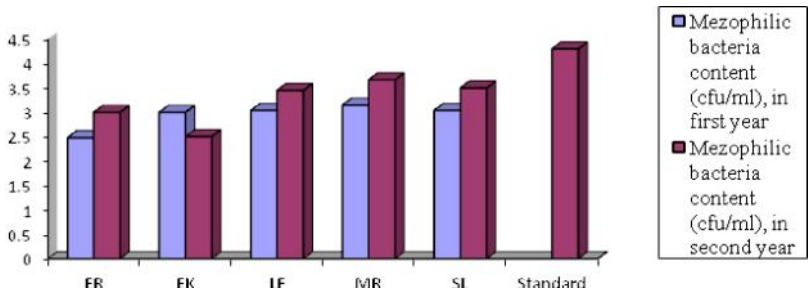

Diagram. 5 The annual comparision of mesophilic microorganisms content for the first day of opening.

In the diagram 5 it is cleatly plotted that the content of mesophilic microorganisms is increased in the second year, except EK samples that have a lower content in the second year. The pH values (first day of opening) remain almost unchangeable throughout the investigation period.

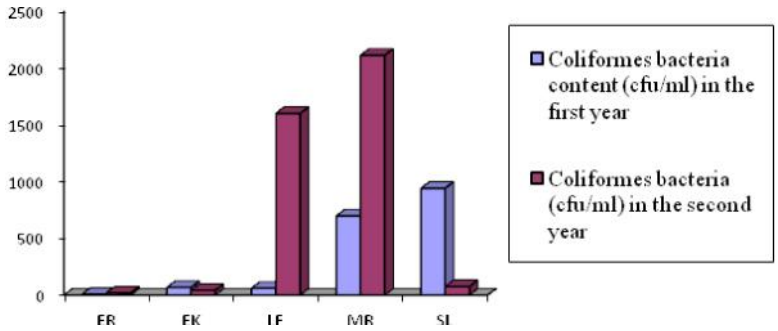

Diagram. 6. The annual comparison comparasion of coliformes.

The second year marks the highest content of coliformes bacteria in the sample LF and MR. However, it is still within permissible limits (<10). The SL sample has a lower content of coliformes in the second year, i.e. the process of ricontamination after pasteurization (as a result of the processing line recontamination or the packaging) is under control (diagram 6).

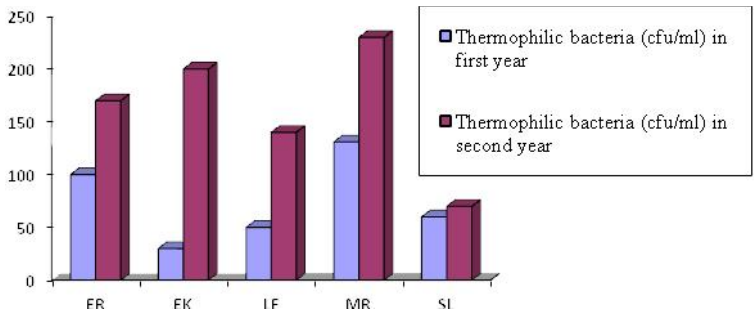

Diagram. 7 The annual comparasion of thermophilic bacteria between the years of investigation.

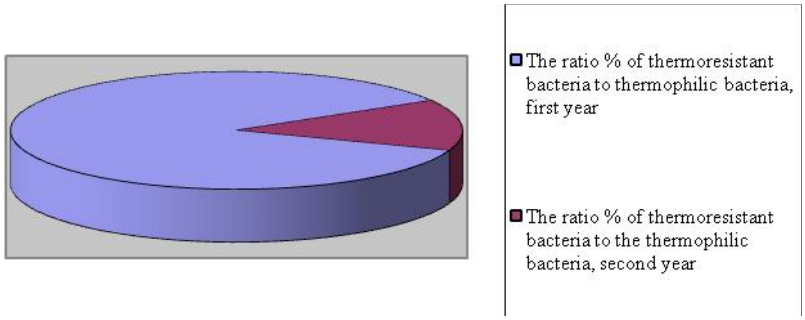

Diagram. 8 The ratio of the thermoresistant bacteria, *B.cereus* to the thermophilic bacteria, in LF sample between two years.

Thermo resistant bacteria consist of thermophilic bacteria (diagram 7). The content of thermo resistant bacteria(*B.cereus*,55%) in the sample LF is higher than in the second year.

4. CONCLUSIONS

Based on the results obtained by alkaline phosphatase and Ruber's test, milk samples were submitted to pasteurization process.

The total bacterial count is within permissible limits. The second year marks for all the samples a higher percentage of bacteria, except for the EK which has lower bacteria content.

The total micro flora has resulted in change of pH and other chemical and physical indicators.

The sample LF and MR have a higher content of coliformes bacteria (within permissible limits) in the second year. SL sample has a lower content of

coliformes in the second year , i.e., the process of recontamination (as a result of the processing line recontamination or the packaging) is under control.

Regarding the LF sample, the thermoresistant bacteria have a higher predominance than the thermophilic bacteria in the first year.

Thermo resistant bacteria like *Bacillus stearothermophilus* are of negative impact for the quality of milk during its storage period. High content of thermoresistant bacteria such as *Bacillus stearothermophilus* shows instability of physic-chemical parameters during the shelf-life of pasteurized milk. Here, acidity changes. In addition, once protein hydrolysis is carried out, lecithin breaks down.

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ASSESMENT CONCETRATION RATE OF HEAVY METALS IN ROASTED COFFEE AND HUMAN CONSUMPTION

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ABSTRACT

The Atomic Absorption Spectrometer (AAS) is in the present investigation used to determine heavy metals concentration rate in roasted coffees. Small amounts of these elements are common in the environment and diet and are actually necessary, but large amounts of any of them may cause acute or chronic toxicity (poisoning). They enter human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial or residential settings. The present paper investigates the concentration rate of heavy metals in roasted coffee and the impact to human consumption. Heavy metal concentration in coffee depends on soil properties and the method used to prepare the coffee. Samples of a blend of Turkish and Espresso coffee were collected from 2010 to 2013 in an Albanian roasting company. The results reported an insignificant concentration of heavy metals in coffee—<0.2 mg/kg. In the Espresso and Turkish phase the quantity of heavy metals, present in liquid, decreased by more 90% in compare with the solid phase.
Keywords: roasted coffee, Turkish and espresso phase, heavy metals

1. INTRODUCTION

Coffee is indigenous to Africa, with Arabica coffee reportedly originating from Ethiopia and robusta from the Atlantic Coast (Kouilou region and in and around Angola) and the Great Lakes region. Today, it is widely grown throughout the tropics. The bulk of the world's coffee, however, is produced in Latin America and in particular in Brazil, which has dominated world production since 1840. For them, coffee exports not only are a vital contributor to foreign exchange earnings, but also account for a significant proportion of tax income and gross domestic product (The Coffee Exporters' Guide 2012).

International Coffee Organization reported that the total production for the 2012 was estimated at around 142 million bags, i.e. the production increased by 2.2%.

The annual per capital consumption is particularly high in Finland (12.0 kg/year) and Sweden (10 kg/year).

Different investigations provide information about the impact coffee consumption to human health. Connor (2005) stated that coffee might soon be considered a health drink following a study showing it as surprisingly rich source of anti-cancer agents. Coffee contributes more antioxidants - which have been linked with fighting heart disease and cancer- to the diet than cranberries, apples or tomatoes. Antioxidants help to rid the body of harmful free radicals, destructive molecules that damage cells and DNA. They have been linked to a number of health benefits, including protection against heart disease and cancer. Studies have associated coffee drinking with a reduced risk of liver and colon cancer, diabetes mellitus type 2, Parkinson's disease and Alzheimer's disease (Gongora-Alfaro 2010; Hjellvik *et al*., 2011).

The two main species currently used are *Coffee Arabica* and *Coffea conphora (robusta*). Arabica beans are considered the most flavorful and in turn command a premium in the market place. Robusta beans tend to be bitterer and less palatable, but they have a 50% higher concentration of caffeine than Arabica beans.

The main process that green coffee undergoes is the roasting process where the green coffee is transformed into a brown soft bean nearly ready for consumption. The reaction brings a lot of physical and chemical changes such as size, structure of the bean, aroma and taste. The volume is doubled and weight and water content lost. The color changes from green to bright, normal or dark brown depending on the type of roasting.

On the other hand, their mineral content remains unchangeable and the relative content increases as water and volatile organic compounds disappear.

The present investigation aims to determine the concentration rate of heavy metals in coffee. The minerals bioaccumulations within the coffee beans depend on trace elements, varieties and environment in which coffee grows.

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. They are individual metals and metal compounds that can impact human health. They are all naturally occurring substances which are often present in the environment at low levels.

Heavy Metal Toxicity

Different investigations provide detailed information about heavy metals and the impact to human health, environment and toxicity (Liu *et al*., 2010; Annete

2006; ATSDR 2007; Santos 2004; Minerals 2008; Heavy Metal Toxicity 2014).

Cobalt (Co) is required for nitrogen fixation in legumes and in root nodules of legumes. It is a part of vitamins B12, an essential vitamin in animal nutrition. In humans, this element appears in most tissues, with the highest amount found in the kidneys, liver, and bones. A high cobalt ion concentration in serum has toxic effects on the heart and liver, but no significant effect on the kidney of mice. The annual demand for cobalt is estimated at 2 mg (Liu *et al*., 2010).

Nickel (Ni) has won the status as an essential trace element for plants according to the Agricultural Research Service Plant, Soil and Nutrition Laboratory in Ithaca, New York (Banerji, 2005). The danger of nickel toxicity from food appears to be very low, since large amounts of nickel are required to produce any toxic effects through ingestion. In contrast to this, in some literature nickel is grouped with toxic metals; Pb and Cd (Dickinson 2006) because contact with nickel or nickel salts cause skin irritations and cancer. The tolerable upper intake level for Ni is 1 mg/day.

Lead (Pb) is a heavy metal commonly occurring in nature. The general population is exposed to lead from air and food in roughly equal proportions. Chronic exposure to lead is associated with multiorgan toxicity. No safe threshold for lead exposure has been determined so far, which means that the amount of lead that can be consumed without it being harmful to the body remains unknown (Rossi 2008). Lead poisoning is known as “plumbism” and is defined by a lead blood concentration above 25 μg/dl for adults (in whole blood) and 5 μg/ dl for children (ATSDR 2007).

Chromium (Cr) is a micronutrient for both plants and animals. In human nutrition the chromium requirement is estimated to be in a range of 50 - 200 μg/ dl. Trivalent chromium is required for maintaining normal glucose metabolism. Evidence shows that chromium improves glucose tolerance. Diabetes and coronary heart disease are associated with low chromium concentrations in human tissue (Santos 2004).

The highest tissue concentrations of **manganese** (Mg) could be observed in liver, kidney, pancreas, and adrenals. Available data clearly show that manganese can cause adverse effects in humans, the most important target being the central nervous system. The recommended dietary allowance (RDA) for manganese is 2.3 mg/day for men and 1.8 mg/day for women (Minerals, 2008). A deficiency can cause poor reproductive performance, growth retardation, abnormal formation of bone and cartilage, and an impaired glucose tolerance (Dietary Mineral, 2008).

Zinc (Zn) is a trace element that is required in the diet. A zinc deficiency causes anemia and retardation of growth and development. Significant excesses are toxic and produce signs similar to lead poisoning. (Heavy Metal Toxicity 2014) The normal range is 0.6-1.1 mg/L (plasma) and 10-14 mg/L (red cells).

Mercury (Hg) is less commonly available around home. It is used in thermometers, thermostats, in certain disinfectants (mercurochrome) and antifungal agents. Mercury is highly toxic when ingested and is even toxic when it contacts skin (Heavy Metal Toxicity, 2014). The toxic concentration of it is 10 µg/L (whole blood) and 20 µg/L (24-h urine)

Both deficiency and exceedance of heavy metals in daily consumption can cause adverse effects on human health. Nutritional status, metabolic rate, the integrity of detoxification pathways (ability to detoxify toxic substances), and the mode and degree of heavy metal exposure all affect how an individual responds. Children and the elderly, whose immune systems are either underdeveloped or age-compromised, are more vulnerable to toxicity.

2. MATERIAL AND METHODS

The blending device is in the present investigation used to mix and homogenize the bulk of roasted coffee sample. An analytical digital balance is used to weigh the coffee samples. Measuring cylinders and micropipettes (Dragonmed, Shangai, China, 100"1000 µl) were used to measure the different volumes of coffee infusion sample, acid reagents and standard solutions.

Volumetric flasks (25 ml, 50 ml, 100 ml) were used for the dilution of the sample solutions and the preparation of standards. Flame atomic absorption spectrophotometer was used to determine the concentrations of heavy metals.

Digestion of the coffee powder: 0.5 g portion of roasted coffee powder, 4 ml of 70% HNO_3 and 0.5 ml of 70% $HClO_4$ were added to a 250 ml round bottom flask which was fitted to a reflux condenser (Gure 2006).Once added, the mixture, was digested on a Kejdahl apparatus for about 2 hours. Once digested, the sample mixture was removed and cooled for 30 min. Once cooled, 30 ml of deionizer water was added.

A filter paper was used during the filtering process to obtain a cleaner solution.

Digestion of liquid coffee: once the coffee extract was prepared applying the Espresso and Turkish method, an aliquot of 25 ml was added to a round bottom flask. Once the samples are cooled, 3.5 ml of 70% HNO_3 and 0.5 ml of 70% $HClO_4$ were added in each flask (Gure 2006). The procedure continued in the same way, as for the digestion of the coffee powder.

Determination of metals in the coffee samples

For the determination of metals in roasted and infusion coffee samples, four series of standard metal solutions were prepared by diluting the stock solutions of the metal with deionizer water. A blank (deionizer water) and standards were run in flame atomic absorption spectrometer (AAS) and four points of

calibration curve were established. All the sample solutions were aspirated into the AAS instrument and direct readings of the metal concentrations were recorded. Three replicate determinations were carried out on each sample. The operating conditions of AAS employed for each analytic are in Table 1 reported.

Table 1. Instrumental operating conditions for determination of some heavy metals using flame atomic absorption spectrometer.

Element	**Cr**	**Co**	**Mn**	**Ni**	**Pb**	**Zn**	**Cd**
λ	357.9	240.7	279.5	232.0	217.0	213.9	228.9
SW	0.7	0.2	5.0	0.2	1.0	0.7	0.7
LC	2.0	4.5	0.2	4.0	5.0	2.0	2.0

λ: Wave length (nm); SW: slit width (nm) and LC: Lamp current (mA).

3. RESULTS AND DISCUSSION

The results of the measurements of heavy metals in coffee powder are in Table 2 reported.

Table 2. Heavy metals present in the Espresso and Turkish coffee powder

No	**Element**	**Espresso Coffee** (mg/kg)	**Turkish Coffee** (mg/kg)
1	Mn	21.97	24.24
2	Co	4.55	4.27
3	Cr	1.03	0.98
4	Ni	7.58	6.06
5	Pb	<0.2	<0.2
6	Zn	7.19	6.88
7	Hg	<0.01	<0.01
8	As	<0.05	<0.05
9	Cd	<0.01	<0.01

Table 2 reports that Mn has the highest concentration both in the Turkish and Espresso coffee powder.

Similarly to our study, a report by (Grembecka *et al.*, 2007) for the microelements shows that toxic microelement Pb, Cd was undetectable even under their analysis.

Many papers provide information about the concentration rate of heavy metals in coffee powder (table 3) (Ashu 2011; Grembecka *et al*., 2007, Santos 2001; Martin 1998). Mangese concentration rate complies with the aforementioned studies. Cobalt concentration rate is higher than in the other studies. Zinc concentration rate is approximate to other studies, except for Uganda. No trace of other elements was detected.

Table 3. Comparison of the concentration rate heavy metals found in different studies for the coffee powder

No	Element	Present Study (mg/kg)	Ethiopia (mg/kg)	Various Origin (mg/kg)	Brazil (mg/kg)	Uganda (mg/kg)
1	Mn	21.97-24.24	22-24	16.5-40.6	4-39	12.1-13.3
2	Co	4.27-4.55	1.3-1.9	0.1-0.9	-	
3	Cr	0.98-1.03				
4	Ni	6.06-7.58				
5	Pb	<0.2				
6	Zn	6.88-7.19	12-19	3.2-16.2	3-15	12.9-57.9
7	Hg	<0.01				
8	As	<0.05				
9	Cd	<0.01				

Extraction of metals with Turkish and Espresso methods

The heavy metals concentration rate in the Espresso and Turkish extract was investigated to determine the amount of their daily intake. The results are in table 4 reported.

Table 4. Heavy metals concentration rate in the espresso and Turkish coffee extracts

No	Element	Espresso Coffee Extract ($^{mg}/_{ml}$ *10^{-3})	Turkish Coffee Extract ($\frac{mg}{ml}$ *10^{-3})
1	Mn	0.72	0.41
2	Co	<0.05	<0.05
3	Cr	<0.05	<0.05
4	Ni	0.21	0.086
5	Pb	<0.2	<0.2
6	Zn	0.13	0.02

The coffee powder has a higher concentration rate of heavy metals than the coffee extracted applying the Turkish and Espresso methods. In line with (Ashu 2011; Gilles 1983; Onianwa 1999; Santos 2001), table 3 shows that the espresso method extracts more elements.

Many papers provide information about the concentration rate of heavy metals

in the extract of espresso and Turkish coffee (Table 4).

The concentration of heavy metals in the espresso and Turkish extract is lower than the quantity of the respective metals in the Espresso and Turkish coffee powder.

The level of Mn is higher in the coffee powder, but still in small amounts. Chromium was undetectable both in Espresso and Turkish extraction. The level of nickel in the Espresso coffee is higher.

Table 5 compares the results of the present investigation with results reported in (Ashu 2011; Gilles 1983; Onianwa 1999; Santos 2001).

Table 5. Comparison of the concentration rate of elements in different studies for the coffee extraction

No	Element	Present study (mg/ml *10^{-3})	Ethiopia (mg/ml *10^{-3})	New Zeland (mg/ml *10^{-3})	Nigeria (mg/ml *10^{-3})	Brazil (mg/ml *10^{-3})
1	Mn	0.41- 0.72	0.2-0.3	0.02-0.16	-	0.29-0.4
2	Zn	0.02- 0.13	0.2-0.3	0.17-0.18	5.6-21	
3	Co	<0.05	0.02-0.024		0.15-21.3	
4	Cr	<0.05				
5	Ni	0.086-0.21				
6	Pb	<0.2			0.14-1.4	0.007-0.009
7	Cd				1.3-10.5	

The concentration rate of heavy metals reported in (Onianwa 1999) is higher than the present results. In addition, presence of Cd was detected. In the present investigation mangnese concentration rate is higher.

Daily intake of heavy metals from coffee.

If an adult consumes three coffees a day and one coffee is around 30 ml, the daily intake of toxic metals such as Mn, Ni and Zn is almost negligible – 50 *10^{-3} mg; 13 *10^{-3} mg and 6.75 *10^{-3} mg respectively.

4. CONCLUSIONS

The industry uses blends of coffee beans, which come from different countries of origin having different organoleptic and chemical properties. The quantity of Arabica or Robusta used in these blends, the level of roasting, coffee processing or the method of extraction, are some of the factors that impact the concentration rate of the heavy metals in the coffee.

The present investigation provides information about the concentration rate of some heavy metals present in the coffee. Five different coffee samples (coffee powder and extracted coffee) were collected and extracted using the

espresso and Turkish method.

Heavy metals concentration rate is higher in the coffee powder than in the extract coffee. Heavy metals such as Pb, As, Hg, Cd were undetectable.

The results here reported are comparable with results of different investigations in the area. Concentration rate is almost negligible.

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A REWIEV OF HUMAN ACTIVITY AND THE DAMAGES TO THE MICRO PRESPA LAKE

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ABSTRACT

Situated in SE Europe, Prespa forms a single high altitude (850 m a.s.l.) tri-border basin shared by Albania, Greece and the Former Yugoslav Republic of Macedonia. The basin covers a total area of 1,519 km^2 and encompasses two interlinked tectonic Lakes - Macro and Micro Prespa - and their surrounding mountains. The region is mentioned for its outstanding biodiversity, natural beauty, good geographical position that make it of great social and economic importance. In addition, Prespa forms a unitary region with rich shared cultural and historical heritage. Archeological sites such as Treni Cave prove that the region has been populated since the Bronze Age. Moreover, it is characterized as wetland of international importance under the Ramsar Convention and the EC Directive on the conservation of wild birds (79/409/ EEC). However, human activity is quite concerning. The present paper reviews on human activity and the damages to the Micro Prespa Lake due to the role it plays in groundwater recharge. The main economic activities are sediment trapping, livestock rising, fishery, forestry and tourism.
Keywords: Macro - Micro Prespa and Ohrid Lakes System, anthropogenic impact.

1. INTRODUCTION

Situated in SE Europe, Prespa forms a single high altitude (850ma.s.l) tri-border basin shared by Albania, Greece and the Former Yugoslav Republic of Macedonia. The basin encompasses two interlinked tectonic Lakes–Micro and

Macro Prespa – and their surrounding mountains. Lake Prespa (altitude 849ma.s.l.) is connected hydrologically with Lake Ohrid (altitude 693ma.s.l.) via underground karstic channels. The region is mentioned for its outstanding biodiversity, landscape, appropriate climatic conditions, good geographic position and historic values. In addition, it consists of complex karst hydrography.

It is characterized as wetland of international importance under the Ramsar Convention and the EC Directive on the conservation of wild birds (79/409/EEC). As anthropogenic impact on the region is quite concerning particularly in the Albanian part of the Micro Prespa Lake, the geophysical complex consisting of remote sensing analysis, hydrographical and limnological studies, hydrogeological, geological, and in particular neotectonic surveys, biological, and environmental investigations was carried out and the results are here reported. Micro Prespa Lake is mentioned for its unique biodiversity and ecologic values.

The later part of the paper provides detailed information about the area and raises awareness for the state institutions and society as general.

2. General setting of the area

Figure 1 depicts the Prespa Lakes and Ohrid Lake which are located at the foot of the mountain Mali i Thatë (2287 m high) and connected with each-other by subterranean channels. The shortest straight line distance between the two lakes is 9 km and Lake Prespa (altitude 850ma.s.l.-962ma. s.l.) is connected hydrologically with Lake Ohrid (altitude 693ma.s.l.) via underground karstic channels.

Fig. 1. Satellite image of Prespa-Ohrid lakes system.

Mentioned for its unique biodiversity and good climatic conditions, the Prespa Lake encompasses Micro Prespa Lake (surface 43 km^2) and Macro Prespa Lake (surface 276 km^2) (Hydrogeological Map of Albania1984; Institute of Hydrometeorology 1984; Bornovas and Rondoyanis 1985; Gligorevich 1988).The catchment area is1¸363 km^2. Figure 2 and photo 1 illustrate the two aforementioned lakes, respectively 55 m and 8m deep—the first lake bordering FYROM (68%), Greece (14%) and Albania (18%), and the second bordering Albania (12.1%) and Greece (87.9%).

In addition to its unique biodiversity, the region is mentioned for its historical values e.g., in Albania, Treni which is a small village on the lake shore of Prespa Lake dates since the Bronze Age.

The region is rich in karst limestone, rugged microrelief, karstic channels, fosses, and caves. The mountains are up to 1456.7 m high in the Micro Prespa region. In the Macro Prespa region they are up to 2035.4 m high. Macro and Micro Prespa Lake catchments are located in a mountainous area. The region is characterized by abrupt changes in elevation within a very short surface area. Dominant values of vertical cutting could be noted at an average level of 100-300 m/km. In the mountainous areas it goes up to 800 m/km (Meçaj 1997).

3. Integrated investigation

Given the importance of the region and enormous anthropogenic impact, the geophysical complex consisting of remote sensing analysis, hydrographical and limniological studies, hydrogeological, geological, and in particular neotectonic surveys, biological, and environmental investigations was carried out.

Multi annual hydrological parameters of the lakes and atmospheric conditions, solid sediment transport from Devolli River at Micro Prespa Lake and anthropogenic activities including: fertilizers and pesticide, waste disposal and industrial waste. Here, investigation of karstic phenomenon and circulation of groundwater through karstic space/underground channels is of irreplaceable importance.

4. Limnological and hydrographic features of Micro Prespa Lake

Minimal and maximal annual precipitation in Korça and Pogradeci basins is 722 mm and 765 mm 1200 and 1000 mm, respectively. The annual average precipitation in Mali Thatë is 900 mm (Fig. 3a) (Chavkalovski1996;Pano *et al.*, 1997; Pano and Frashëri 1999; 2000 a,b,c; Pano *et al.*, 2000; Pano *et al*., 2004; 2003 a, b). Here, effective infiltration is 455 mm. Evo-transpiration is 426 mm. The water volume of the karst spring flowing from Mali iThatë is 5.2 m^3/sec or 165.2x106 m^3/year. Water discharged into the karstic limestone of Mali iThatë.

Micro Prespa - Macro Prespa system represents the largest and the most important limnological entity both for its big water capacity and ecological values.

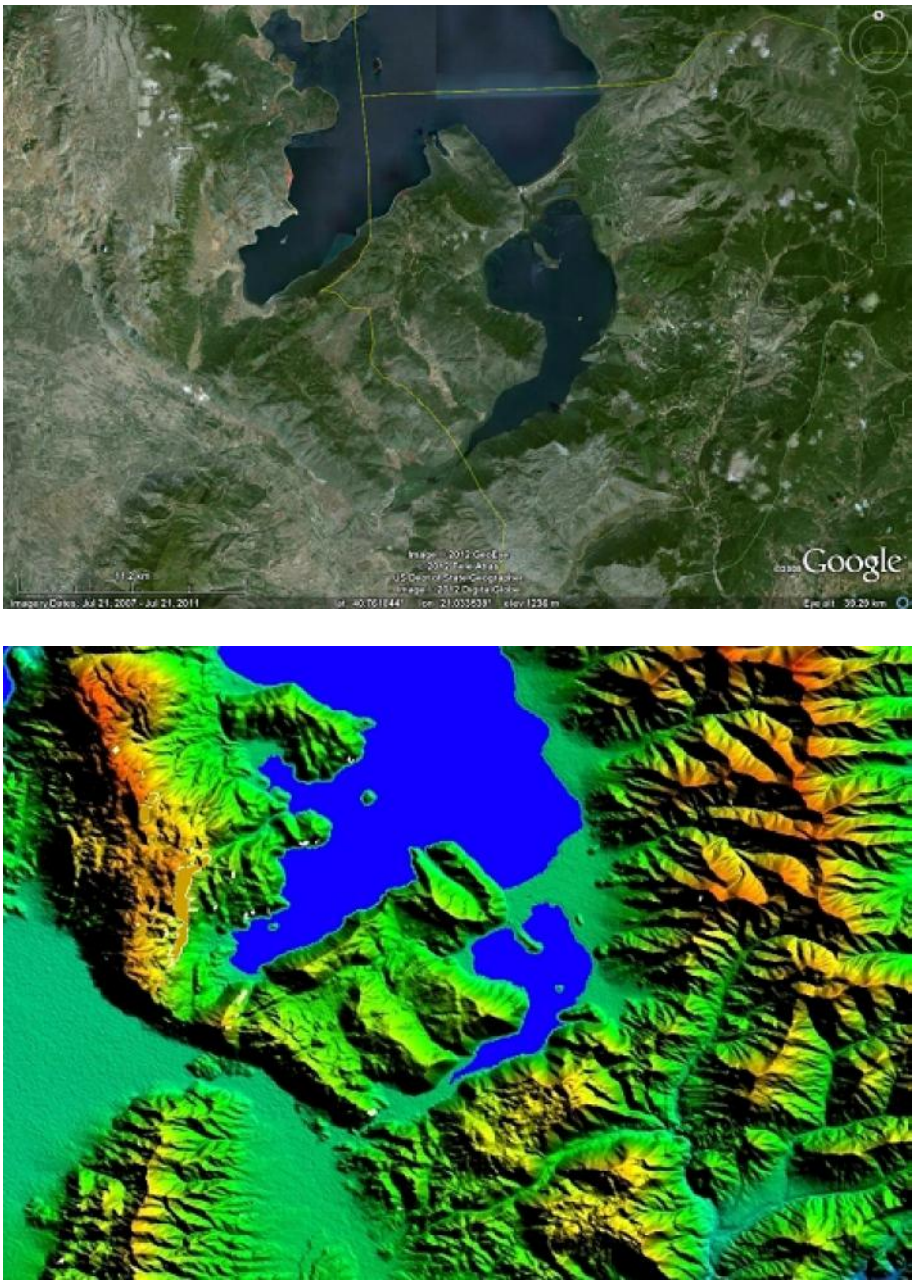
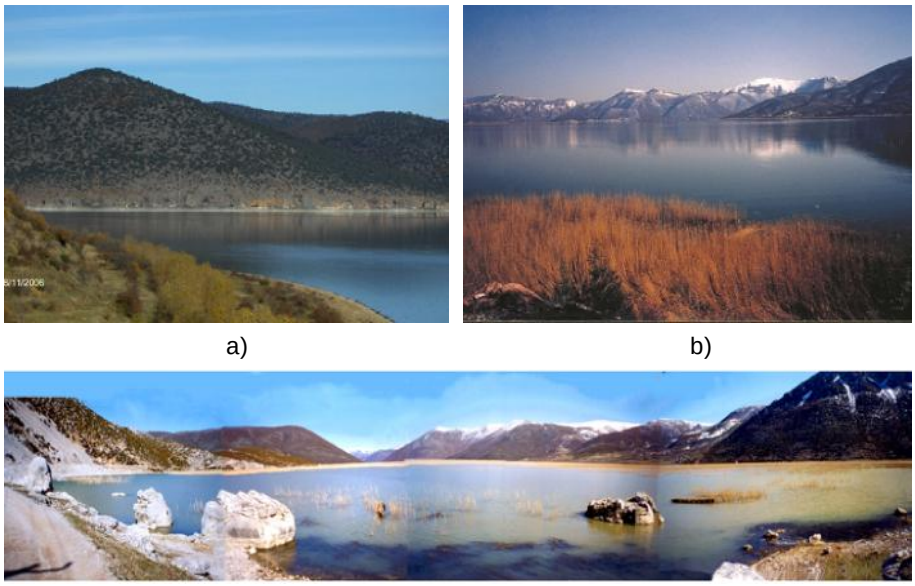


Fig. 2. Top – Satellite image of Micro Prespa Lake. Bottom – its Digital Terrain Model based in SRTM

Figure 2 and photo 1a-c depict the Micro Prespa Lake and Macro Prespa Lake. The two lakes are of great hydrographic importance and have a NW-SE extension. In Albania, the shoreline of Micro Prespa Lake is 5.75 km. Its minimum width is 125 m on the southeast in Gryka e Ujkut. Its maximum width goes up to 1500 m, between Shuec and Buzë Liqeni villages.

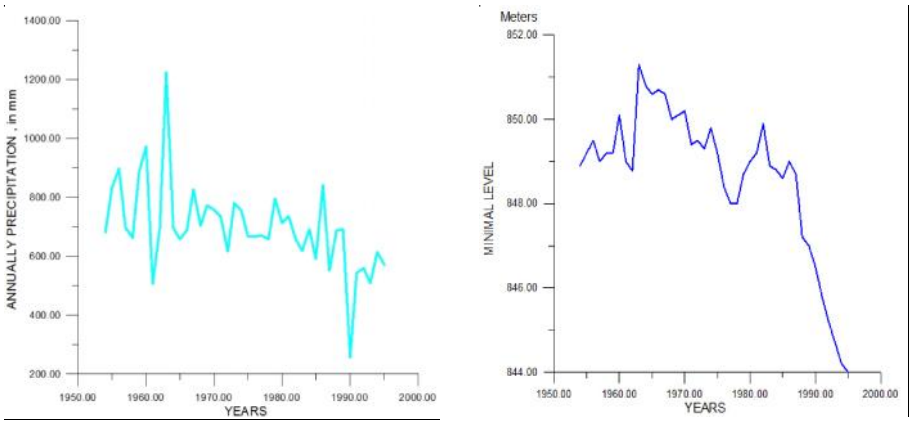


a) b)

c)

Photo 1. Prespa Lakes system: a) Macro Prespa; b) and c) Micro Prespa 2006.

Long-time sediments transport by the Saint German (St. German) River flowing from Varnoundas Mountain in Greece and sediment deposits divided the Lake Prespa into the Micro Prespa Lake and Macro Prespa Lake. The straight-line distance between the two lakes is 3 km long and 1.2 km wide. Figure 2 and photo 2 depict the channel and the underground karst aquifers, which connect the two lakes with each other. Micro Prespa water flows into Macro Prespa Lake through this channel. The two lakes exhibit distinct lake level fluctuation. Macro Prespa Lake has recently marked the greatest decrease in the water level (Institute of Hydrometeorology, 1984; Chavkalovski 1996; Pano and Frashëri 2000 a, b,c; Pano *et al*., 2000;Pano *et al*., 2004; 2003 a,b) (Fig. 3b).



a) b)

Fig. 3. Average annual precipitation in Pretori village, and average annual minimal water level (b), Macedonia (see Chavkalovski, 1996).

The lake loses annually about $150x10^3$ $m^3$of water. The water level of Micro Prespa Lake is +850 m. Currently, the water level in the Macro Prespa Lake is +846 m. The period running from 1987 to 1990 marked a drop by 7 meters, i.e., 900 million m^3 in the water level of Macro Prespa Lake.

Photo 2. The discharge of Micro Prespa Lake water into Macro Prespa Lake, through the channel in Greece, 2000.

Photo 3. Karstic activity, Macro Prespa Lake, 2006.

Macro Prespa Lake is mentioned for its light blue, deep and clear water - up to 20 m deep. In summer the temperature of the water temperature goes up to 24°C and in winter it goes up to 0.4°C. Some torrent flow in the eastern part of Macro Prespa and there is not any surface emissary. Intensive water discharges have occurred through underground channels and some karstic springs in Devolli plain mainly in Lake Ohrid which is located 145 m below lower. Lake Macro Prespa water discharged into karstic limestone of Mali i

Thatë—a phenomenon occurring particularly near Gollomboçi village (Photo 3 and4). Photo 5 illustrates the current situation of the Lake Micro Prespa. The water of the lake became turbid by the end of the 20thcentury.

Photo 4. Point of the disappearing Macro Prespa water, which migrated to Ohrid Lake (from Google Earth).

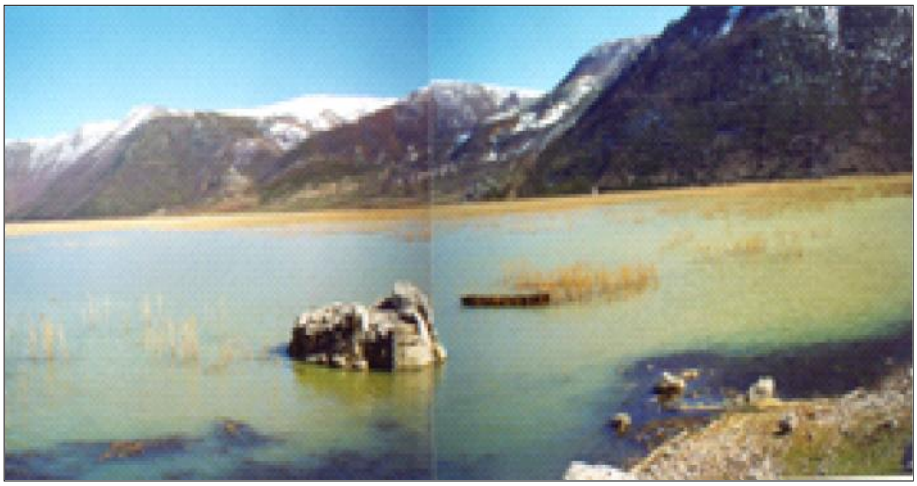


Photo 5. Troubles waters in Micro Prespa Lake, 2000.

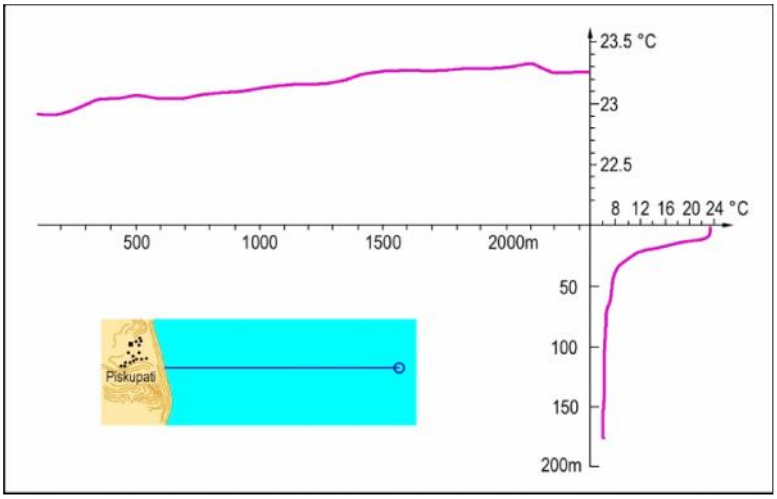


Fig. 4. Water temperature of Ohrid lake.

Lake Ohrid is shared by Albania (30%) and FYROM (70%). It is a tectonic lake formed during the Upper Miocene. Currently, its surface area is 358 km^2. It has a maximum water depth of 289 m, mean water depth of 155 m, and volume of 55 km^3 (Matzinger *et al.*, 2006). In 1979, the Ohrid Lake was inscribed on the World Heritage List. Figure 4 depicts the temperature profile of the water.

Mali Thatë (2280m) separates Ohrid and Prespa Lake. Isotopic hydrogeological investigations report the same content of the 18O isotope of the oxygen and deuterium in the Ohrid and Prespa Lakes, and Tushemishti and Saint Naum springs (Eftimi and Zoto 1997). Initially supposed by Cvijić (1909) and latter investigated by (Institute of Hydrometeorology 1984) Prespa Lake recharges the St. Naum and Tushemisht springs at the Ohrid lakeside. Environmental isotopes demonstrated that Prespa Lake recharges about 37–42 and 52–54% of water emerging in St. Naum, and Tushemisht springs, respectively.

5. Underground waters resources

Prespa region is rich in subterranean water resources which are connected with Prespa lakes, massive karstified limestone of Mali i Thatë and the precipitation water infiltration into karstified limestone (Hydrogeological Map of Albania 1984; Institute of Hydrometeorology 1984). Isotopic Œ^{18}O (in %O) hydrogeological studies reported that the average height of the precipitation infiltrating into Mali i Thatë is 1130 m (Efthimi and Zoto1997).

In the western slope of Mali i Thatë, from Progër village to Tushemisht village, there is a series of karstic springs. Very developed underground karstic

channels determine their yield. The springs in Gollobordë, Mançurishtë and Progër exhibit the highest yield rate of about 500-600 l/sec. Springs or springs groups which water yield is about 1 to 100 l/sec are located 2 km from each other. Strong springs of Tushemishti with a yield of about 2 500 l/sec are located on the north in Ohrid lakeshore. Alluvial sediments in Micro Prespa Lake floor has closed the *subterranean* water flow channels of some springs that have an elevation below the lake level (Pano and Frashëri1999; 2000 a, b, c; Pano *et al*., 2000). Recent investigations reported considerable reduction in yield for some springs.

There are artesian water basins in Devolli and Korça plains. The Quaternary gravel deposits of old river terraces, covered by clay's layers, represent their water horizon.

6. A review of geological profile of the region

Prespa Lakes are located in the piedmont carbonate structure of Mali i Thatë (Geological Map of Albania, 2002; Tectonic Map of Albania 1986; Pano and Frashëri 1999; 2000 a, b, c Pano *et al*., 2000; Pano and Pano *et al*., 2004; 2003 a,b). This carbonate structure presents a horst of Upper Triassic and Lower Jurassic age limestone (Fig. 5). Intensive tectonic development has been carried out on Triassic-Jurassic limestone. Upper Cretaceous limestone and Middle Eocene flysch clay in some sectors of the region. The northwest of Macro Prespa Lake consists of Pliocene clay and sandstone deposits. Placers deposits, clay, argillite, clay sand, sand, gravel, cobbles, broken stone of recent Quaternary overlay the Pliocene clay-sandstone and Eocene flysch lakeshores. Some sectors consist of proluvial deposits (Mankolli *et al*., 2006). Ultrabasic rock individualization which has a tectonic contact with limestone interrupts the Albanian part of Micro Prespa Lake.

A Pliocene terrigenous continental deposit have been deposited in the inter-mountain lakes and in the deltas of the rivers, which was flowed in these lakes. Consequently, once neotectonic developments occurred, contrast relations of the uplifts and plunges followed and the depression where sediment deposits locate has been created (Fig. 5) (Aliaj *et al*., 1995; Hyseni *et al*., 1999; Pano and Frashëri 2000 a,b,c, Pano *et al*., 2000 ; Pano *et al*., 2003 a, b; 2004). These lakes were formed from Pliocene to Holocene. Karst process activity was developed at the same time (Photo 3). Tectonic and karst played a great role in forming Macro and Micro Prespa lakes.

Considerable amounts of alluvial sediments have been deposited at the bottom of the lakes due to intensive erosion occurred in the Prespa region.

Geological setting is the main factor that conditioned lakeshore stability of the Prespa lakes. High and abrupt lakeshores are located at limestones sectors (Fig. 5, 6). The abrupt lakeshores (10 to 50 m high) are located generally in the

southwest of Micro Prespa Lake. Spilea rocks are located in the north of Gryka e Ujkut. Their height goes up to 1150 meters. There some precipices found which height varies from 10 to 50 meters. The lakeshores in the Quaternary, Pliocene clay-sand deposits or Eocene flysch sectors, and in particular in the slope breccias sectors are unstable. In shore sectors, the slopes are some meters away from the lakeshores. There is a gravel belt between them. In the lakeshores of Prespa Lakes, flow's cones of the mountain's streams which are dry in summer could be met.

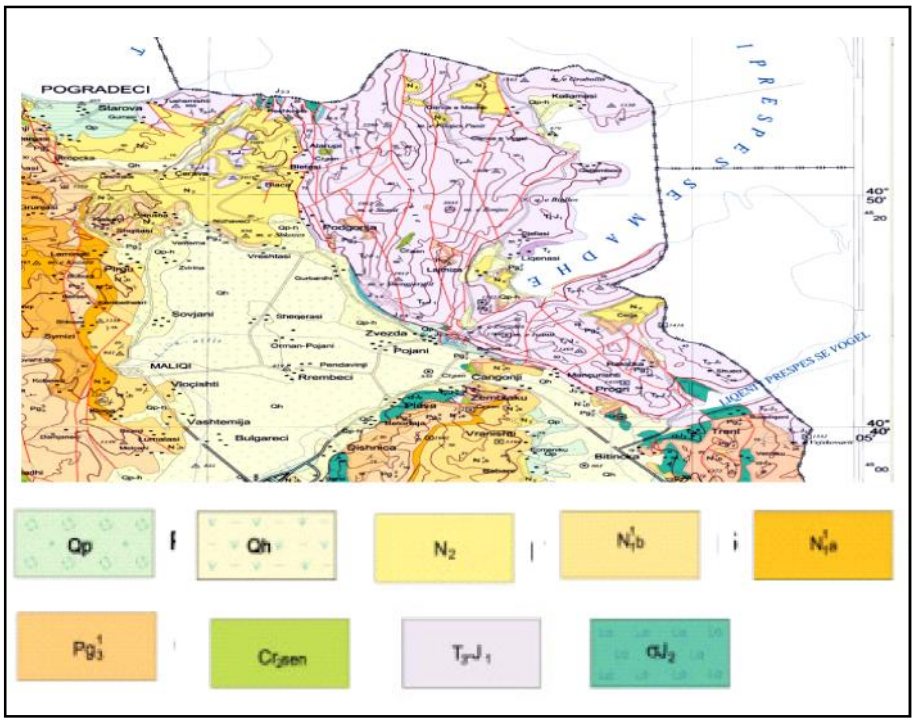


Fig.5. Geological Map ofPrespa lakes-Ohrid Lake area. (Geological Map of Albania2002, at scale 1:200.000). 1. Holocene- alluvion, proluvion, lacustrine, aleurolite, sand, gravel; 2- Holocene- swap deposits, clay, sand peat; 3- Pliocene- clay, sandstone, gravelite, conglomerate; 4- Burdigalian- clay marl, siltstone, limestone, limestone; 5- Aquitanian- sandstone, siltstone, conglomerate; 6- Lower Oligocene- muddy and siltstone flysch, limestone; 7- Upper Cretaceous, Senomian- limestone, conglomeratic limestone; 8- Upper Triassic-Lower Jurassic- Limestone, dolomite; 9-Ophiolite.

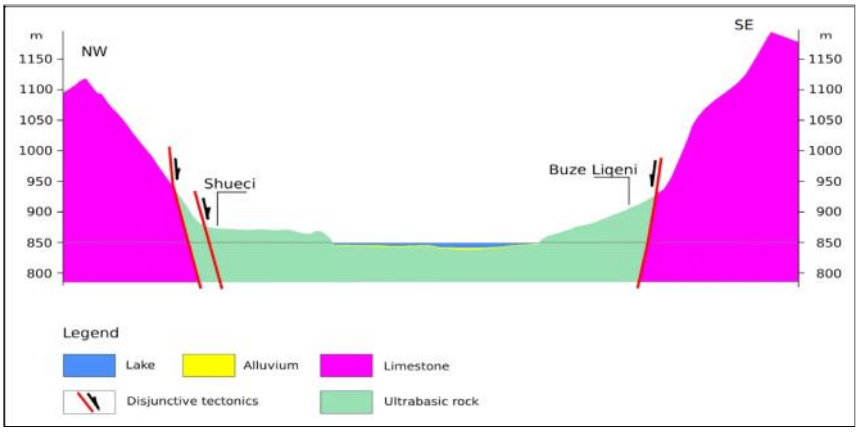


Fig. 6. Geological Profile through Micro Prespa Lake.

Mineral deposits in the Prespa region, in particularly industrial materials (construction materials) are genetically related to the geological setting of the region. The region is rich in quartzose sand and clay. Construction materials of high quality found in the region consist of limestone and ultrabasic rocks.

7. Biodiversity and present legal protection status

Many investigations provide detailed information about the biodiversity of Lake Micro Prespa (Pano *et al*., 1997; Bega 2000; Bino 2000; Pepo 2000; Qoshja 1979; Rakaj 2000; Shumka 2000).

In the Prespa region there are71 tree species and shrubby trees.

The following plants species are found in the aquatic bed: *Caratophyllum* sp., *Myriophyllum* sp., *Lemna minor*, *Trapa Natans*, *Nymphaea* Alban, etc. The trees species are: *Salix*sp, *Querqus cerris, Querqus pubescens, Querqus Petrea, Fagus silvatica, Oatria Caprinifolia, Fraxinus Ornus, Carpinus Betulus, Acer pseudoplantanus, Pinus nigra, Abies, Junglans regia, Castanea sativa, Corulys, Juniperus*, etc. In addition, oak forests in Maja e Zonjës, Maja e Kallogjerit and Faqes së Osojës in Makro Prespa region and Koria e Trenit in Micro Prespa region are an added value for ecosystem of the region. Moreover, the emergent species could be found: *Carex* sp., *Trifolium* sp., *Phragmites australis*, *Tupha* sp., *Scirpus* sp., etc.

The fauna of the Prespa Lakes is mentioned for the following rare fish species*: Rutilus prespensis, Chordrostoma prespensis, Barbus prespensis, Albumus belvica, Albumoides binpunctatus orhiadanus, Cobitis meridionalis, Cyprinus carpio, Salmotrutta peristericus*, etc. Bird species are: *Pelecanus criptus* Bruch (Photo 6 a,b), *Pelecanus onoctotalus, Pholacrocorax pygmeus*, Ardea *purpurea, Plegadis falcinellus, Egretta alba, Platalea*

leucorodian Anseranser. Mammals such as *Rhinolophus ferrumequinum, Pipistrellus nathussi, Glis glis, Canis lupus*, C. *aureus, Lutra lutra, Felix silvestris, Meles meles, Ursus arctos,* etc. could be found. The *Polygonetum amphibii* is a very sparse association of the Prespa lakes. *Potameto-Najadetum H.* could be met in the Macro Prespa region.

The pelagic zooplankton community of Micro Prespa Lake consists of 43 species. The zooplankton community of the region comprises Protozoa-1 specie, Ritatoria-16 species, Cladocera-16 species, Copepoda-9 species and Mollusca-1 specie.

Photo 6 a, b. *Pelecanus Criptus* Bruch.

Prespa Lakes catchments are mentioned for their unique geomorphology, ecological system, and biodiversity, which give the area significant international importance. It is characterized as wetland of international importance under the Ramsar Convention, the EC Directive on the conservation of wild birds (79/409/EEC) and Important Bird Area (ICBP-IWRB). The ecological importance of both lakes was acknowledged by the declaration of Lake Ohrid

as UNESCO world heritage site in 1979 and by the establishment of the Prespa National Park in 1999. Increasing human population in both lake catchments, eutrophication of the lake waters, and ongoing use of lake water for agriculture are adversely affecting the ecosystems today (Matzinger *et al*., 2006; Kostoski *et al*., 2010).

8. Historical heritage of Prespa

The Prespa region has been settled since bronze and Neolithic ages. Devolli and Pogradec regions have been inhabited by Encheleana an Illyrian tribe from 1500-1400 BC (History of Albania 1959; Samsuri 2000). Treni cave is located on lakeshore of Micro Prespa Lake. It proves that the region has been populated since Bronze Age. Other archaeological data provide information about the Early and Late Bronze Age and Iron Age. Photo 8 illustrates prehistoric rock drawings found on Spilies rocks, on the northern lakeshore of Micro Prespa. In addition, the region is mentioned for its Byzantine monuments of the 18th-19th century and traditional architecture. The most important Byzantine monument is the St Mary Church built in the 14th century in Grad Mountain Island in Macro Prespa Lake. The first towns were founded from 851-1018 and Devolli was the capital by the time. By the end of 10th century Prespa and Ohrid become important centres of the Bulgarian Empire.

Photo 7. Prehistoric Treni cave on the lake shore of Micro Prespa Lake.

Photo 8. Prehistoric ancient designs at the Spilea rocks, on Micro Prespa lakeshore (after Grazhdani 2000).

9. Anthropogenic impact

Unfortunately, the ecosystem of the region has been threatened by intense human activity. In Albania, human activity including construction of hydro-technical works such as network channel in 1976 for irrigation of plains in Devolli and Korca (fig. 7), water supply of Micro Prespa Lake with Devolli River water (photo 9) have been devastating for the equilibrium and biodiversity of Micro Prespa Lake (Pano and Frashëri 2000a,b,c, Pano *et al*., 2000).

While parts of the lakes ecosystem have been changed to better suit the needs of humans, the unexpected consequences of many of the changes have only recently become apparent. The largest categories of impact are pollution and habitat loss. Habitat loss and deterioration in water quality have caused serious threat to plants and animal species in the last five years.

Uncontrolled timber harvesting and over grazing have resulted in degradation deforestation of the forest resources and serious erosion.

Uncontrolled fishing and hunting are a continuous threat to extension for the fish species.

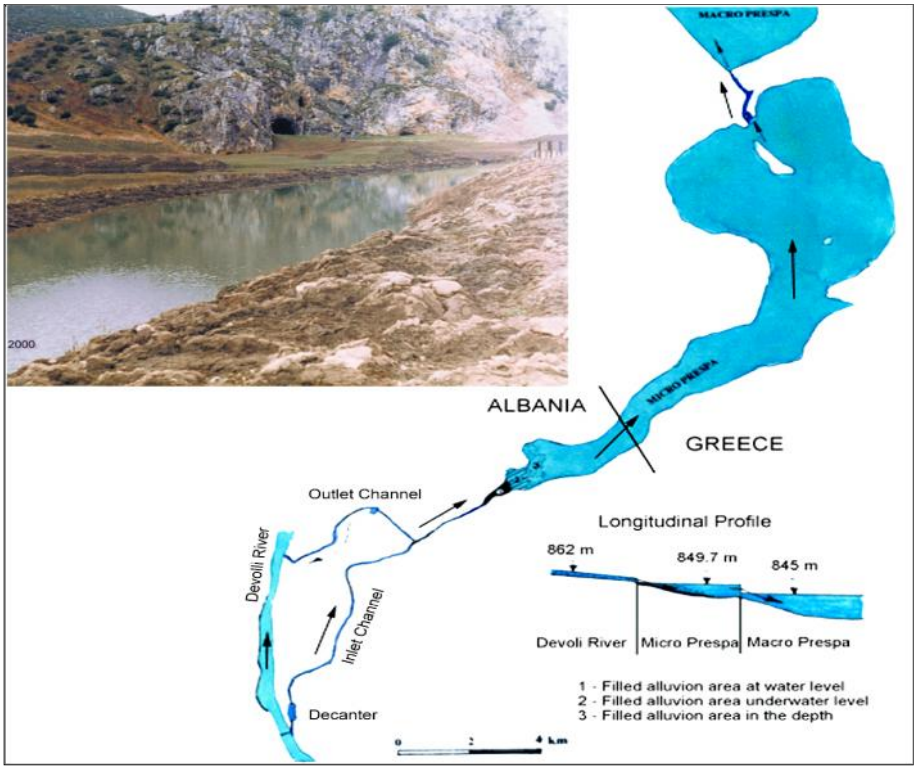


Fig. 7 Water Supply and Irrigation System Sketch from Devolli River to the Micro Prespa Lake and water flow to the Macro Prespa Lake. Top – Left: photo of the channel that supplied Micro Prespa Lake with Devolli River water.

9.1. The impact of the hydro-technical constructions on the ecology of the Micro Prespa Lake.

Constructed in 1976, the channel which water capacity is Q=10 m^3/sec to supplies Micro Prespa Lake with Devolli River water in winter (Fig. 7). Annually, 30-70 million m^3water per year is discharged into Micro Prespa Lake through this channel. According to the project, the maximal water hyplometric level in the lake would be 852.2 m at the end of the supply period. In summer, the lake water is used for irrigation purposes in Korça and Devolli plains with a total surface of 22 500 ha. The maximal quote of exploitation according to the project is 850.2 m^3, but 90 million m^3 water are currently used.

Devolli River is one of the most turbid rivers in the Balkans. The water of the river has a mean mineralization M = 483 mg/l and a hardness 12 German degree. Granules with a diameter less than 0.02 mm predominate in this sediment. Fourteen percent of the sediment mass consists of granules with a diameter less than 0.002 mm. According to the American Classification ASTM,

this sediment is classified as Lean Clay CL. Their plasticity index Ip=13.5, and the upper and lower limit of plasticity, respectively Wl= 42.2% and Wp=28.7 %, show that the clay material comprises illite and montmorillonite. A considerable amount of its water flows into Micro Prespa Lake in winter. A substantial amount of solid matter has been transported and deposited into the Prespa Lake. Consequently, the lake plays the role of an authentic gigantic decanter (Photo 10a- c).

A decanter has been constructed to avoid alluvial sediments. Unfortunately, the decanter has not been put into function. Results of the investigation reported that Devolli River water flows undecanted into Micro Prespa Lake, depositing about 1.2 million m^3 of alluvium, diminishing the water volume, the water surface of the lake and depredating its ecological values. Once the decanter is put into function, and the lake is free of alluvial deposits

No scientific evidences, environmental engineering and hydro-economical and international laws were followed when constructing the irrigation system Devolli River-Micro Prespa Lake. In addition, it does not work according to parameters established and the current needs of the agricultural are not met. Less than 10% of the water discharged into the lake has been used for irrigation and water supply purposes. In 1997, only 2.3 million m^3out of 90 million m^3 (defined in the project) was used. In 1998 and in 1999, only 5 million m^3 out of 90 million m^3or 0.4 m^3/sec out of from 10 m^3/sec was used because Micro Prespa Lake communicates with Macro Prespa Lake (Fig. 7, Photo 1c). In these conditions turbid water of Devolli River upon flowing in Micro Prespa Lake decant in it, ruining it. Once free of alluvial deposits, the river flows into Macro Prespa Lake.

9.2. Damages of the biodiversity

Eutrophication process is quite concerning for the Micro Prespa Lake (Photo 1c, 11a and b, 12). It is the enrichment of an ecosystem with chemical nutrients, typically compounds containing nitrogen, phosphorus or both of them. Many papers provide information about the impact of eutrophication to the biodiversity (Qoshja 1979; Pano *et al*., 1997; Bega 2000; Bino 2000; Pano and Frashëri 2000 a, b, c; Pano *et al*., 2000; Pano *et al*., 2003 a, b; 2004; Pepo 2000; Rakaj 2000; Shumka 2000).

Toxic elements are present in the region due to anthropogenic activities, with fertilizers and pesticides applied in agricultural activities in the region and outcrop of geological section.

The lake is rich in nitrite, nitrate, ammoniac, phosphate, carbonate, and organic material. Changes in water chemistry could be noted within hundred meters from the southwest of the lakeshore to some meters deep (Kanari 2000). This changes the lake water features and degrades their habitats.

Habitat loss and deterioration of over the last five years are the major factors causing serious threat to plants and animal species. In particular, this phenomenon obviously influences a part of the aquatic flora and fauna in the lake.

Photo 11. Eutrophication of the Micro Prespa Lake water, 2000.

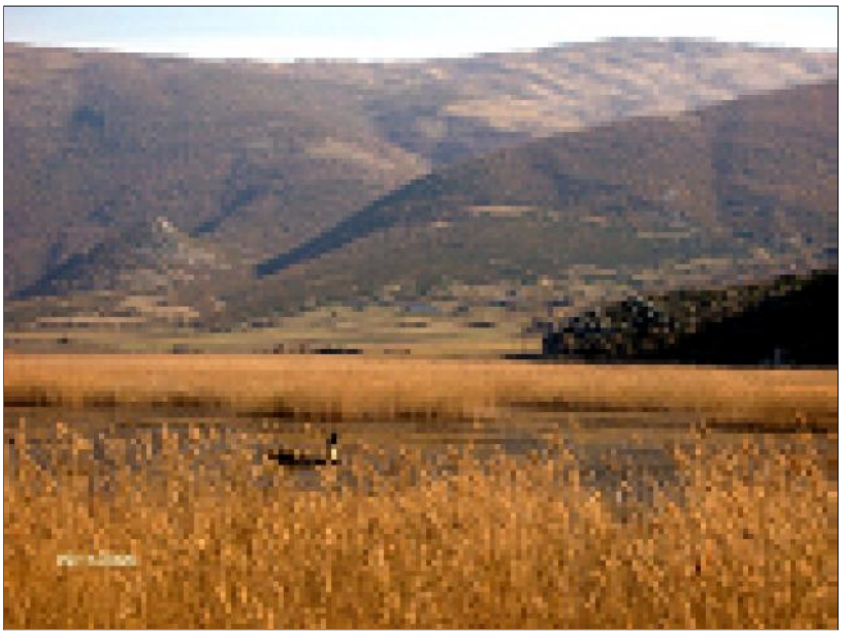


Photo 12. Eutrophication of the Micro Prespa Lake water, 2006.

9.3. Threaten flora

Anthropogenic activity has dramatically damaged the aquatic bed plants like *Nymphaea Alban, Caratophyllum* sp., *Myriophyllum* sp., *Lemna minor, Trapa natans, Leucojo-Fraxinetum Angustifobiliae, Potameto-Wallisnerietum, Nymphoidetum peltatae* etc., and tree species such as *Carpinus betulus, Acer pseudo plantanus, Corulys*, etc.

9.4. Threaten Fauna

In addition to flora, anthropogenic activity has been of great damage for the fish species such like *Leuciscus Illyricus; Salmotrutta Peristeris and Barbus Prespensis*. Eutrophication process has greatly damaged zooplankton composition of the Lake.

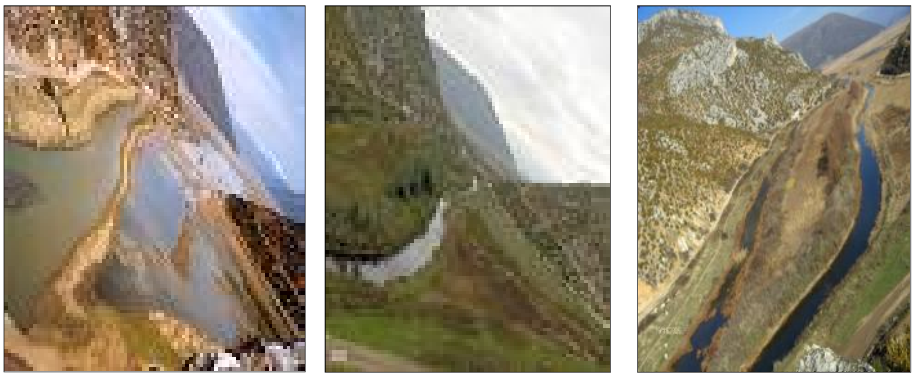


Photo 10. General view of the damages caused to ecosystem at the Prespa Lake shore, (a) 2000, (b); (c) 2006 .

9.5. Subterranean water resources and springs

Lacustrine alluvium has coated all shallows of Micro Prespa lakeside and blocked its underground water resources. Consequently, the water balance of Micro Prespa Lake is destroyed and the yield of drinkable water springs yield has diminished. The water discharge of Ventrok spring was 13.8 l/sec before the lake was filled with sediments. Unfortunately, the spring is drying up.

Assessment of environmental situation in Micro Prespa Lake using Landsat images

Environmental situation was investigated using Landsat images of 1972 (1973 for the NIr band), 1987, 2002 and 2010. The following methods were applied to investigate the situation of the vegetation: i) annual natural colour combination of blue, green and red, enhancing the colours in water surfaces in order to make visible water turbulence. Enhancement of colours was done keeping as reference the Ohrid Lake, which water did not show any sign of turbulence, ii)

combination in false colours of NIr bands in two ways: 1973~Blue, 1987~Green, 2002~Red and 1987~Blue, 2002~Green, 2010~Red. Such combinations were used to identify variations of lakes shores and, iii) combination in false colours of NDVI in two ways— 1973~Blue, 1987~Green, 2002~Red and 1987~Blue, 2002~Green, 2010~Red (Frashëri *et al*., 2010).

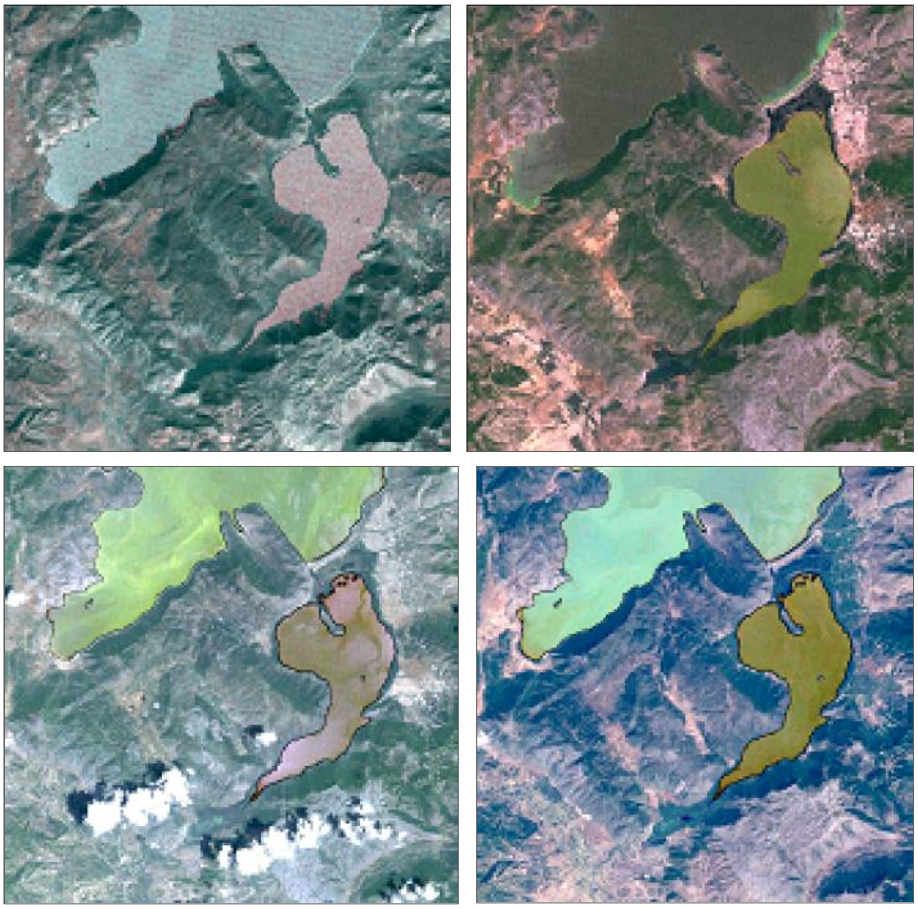


Fig. Aaa – Natural enhanced colours of Macro and Micro Prespa Lakes (top left ~ 1972, top right ~ 1987, bottom left ~ 2002, bottom right ~ 2010).

There was no significant turbulence in the lakes in 1972. Water of Micro Prespa looked more "reddish" as it was shallower. The first signs of turbulences in Micro Prespa Lake and near shores of Macro Prespa Lake were marked in 1978. Situation resulted dramatic in 2002. However, little improvement was shown in 2010 as water flow from River Devolli was interrupted in the South-western corner of Micro Prespa. Here, the colours are not enhanced (Frashëri *et al*., 2010).

The figure 12 depicts the South-western corner of Micro Prespa Lake rich in vegetation —mostly reeds—except for a small area in its centre (Frashëri *et al*., 2010).

Fig.Bbb – Google Earth image of South-western corner of Micro Prespa Lake. Villages of Shueci and Buzë Liqeni are shown as markers for the geological profile of the Lake.

At the bottom-left corner of the image, the channel where the Devolli River flows into the Lake during winter time could be noted.

The variation of lakes shores was done comparing NIr images by combining them using false colours. Permanent water areas appear in black, permanent ground areas in gray or nuances having all three RGB base colours, while areas where the shore line has moved, appear in specific colours with only one or two components of base colours.

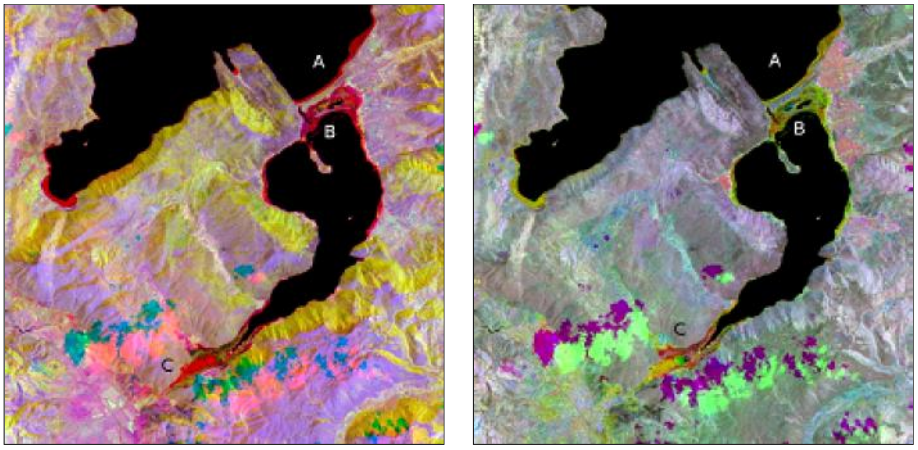


Fig Ccc – Combination of NIr bands (left: 1973-1987-2002, right 1987-2002-2010)

Combining 1973 (blue) – 1987 (green) – 2002 (red), part of Macro Prespa Lake shore ("A"), the Northern shore ("B") and the South-western corner of Micro Prespa ("C") appear in clear red color, reporting loss of water surface events from 1987 to 2002. In addition, Macro Prespa Lake marked a decrease of water level and Micro Prespa Lake was characterized by sedimentation and increase of reeds. Combining 1987(blue) – 2002 (green) – 2010(red), the same areas show lack of red component, indicating that during 2002–2010 there was no change in the shore line. In the area A, some reddish spots could be noted due to the development of reeds and in its centre. The green spot indicates that the area was filled with reeds in 2002. Consequently, the water quality improved in 2010.

The variations in time of NDVI are presented with false colours in the following figure:

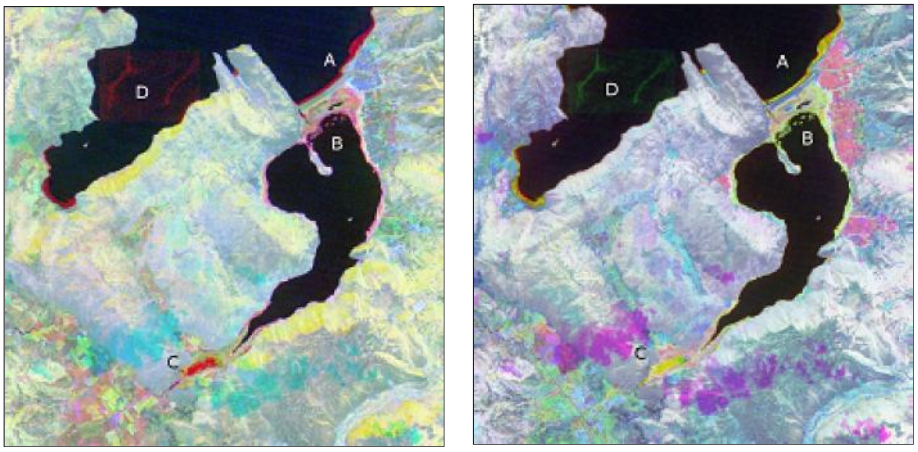


Fig Ddd – Combination of NDVI (left: 1973-1987-2002, right 1987-2002-2010).

The same phenomena could be noted in false color combinations of NDVI for the two periods 1972(blue) – 1987(green) – 2002(red) and 1987(blue) – 2002(green) – 2010(red). The environmental situation in both Macro and Micro Prespa Lakes has deteriorated from 1987 to 2002. However, a slight improvement could be noted from 2002 to 2010, due to interruption of water loss in Macro Prespa and Devolli River water flow in Micro Prespa. The area indicated by "D" shows strips of algae developed in Macro Prespa waters in 2002.

10. CONCLUSIONS

Prespa Lakes belong to a group of Dasseretes basins that originated from a geotectonic depression 2 to 3 million years ago on the western Dinarides. The region is mentioned for its unique biodiversity, natural beauty, good geographical position that make it of great social and economic importance. In addition, Prespa forms a unitary region with rich shared cultural and historical heritage. It is of international importance under the Ramsar Convention and the EC Directive on the conservation of wild birds (79/409/EEC). The outstanding degree of biodiversity, on one side, and the "creeping biodiversity crises" in lakes Prespa, on the other side, have spurred the geophysical complex consisting of remote sensing analysis, hydrographical and limniological studies, hydrogeological, geological, and in particular neotectonics surveys, biological, and environmental investigations. The following conclusions are drawn: i) lack of environmental engineering and hydro-economic studies when constructing the irrigation system. Consequently, the irrigation system does not fulfil the criteria for a good functioning, and the basis of the population is not provided, ii) in Albania, considerable surface of Micro Prespa Lake is damaged. In Macedonia, the lake is atrophied. In addition, the region is characterized by degraded habitats and declined biodiversity. Consequently, flora and fauna of the lake is endangered. Subterranean karstic channels for water flow are blocked, iii) transported by Devolli River, 1,2 million m^3 alluvium have been deposited at the bottom of the lake and lakeshore since in 1974. The River is rich in alluvium and organic coal material due to the outcropped geological formations and absorbed free chemical toxic residues by the drainage of Devolli farm ground. Consequently, chemical content of the water changed. Micro Prespa Lake communicates with Macro Prespa Lake and Ohrid Lake. Components of the lake water balance have been diminished and underground springs decreased their yield due to blockage of underground karstic connection channels that supply the Ohrid Lake and drinkable water springs. The Albanian part of the Micro Prespa Lake plays the role of a gigantic decanter, iv) alluvium deposits in Micro Prespa Lake diversified the ecosystem in this area.

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OPENING AN UNDERGROUND GAS STORAGE IN THE DUMRE REGION

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ABSTRACT

There is a continuous demand for gas consumption in Albania. Unfortunately, recoverable natural gas reserves and current daily production are limited. Consequently, increasing gas production from existing fields, exploring new gas fields and connecting the existing Albanian gas pipeline with the European network through Trans Adriatic Pipeline are quite challenging. On the other hand, seasonal fluctuations for gas consumption and the needs of Kosovo and FYROM for gas supply, opening underground gas storages in the salt domes of Dumre region and extending gas pipeline to these neighboring countries is of immediate importance.
Keywords: natural gas, storage, salt, supply

1. INTRODUCTION

The natural and associated gas in Albania have been mainly used in the industrial plants of Ballsh, Fier, Vlora, Elbasan, Berat, Durrës, and Kavajë region and in small quantities for communal consumption in Kuçova and Patos. However, gas production has dramatically decreased by the end of 1984, making gas supply of the Fertilizers Plant of Fieri, Oil Processing Refinery in Ballsh and the other industrial entities difficult. Since then, daily production meets only the needs of few communal manufactories and population of Kuçova and Patosi region and the oil field equipments and nappe gas injector. Consequently,

accurate investigations on new gas storages, the recovery of the Albanian gas pipeline network and its connection with the Trans Adriatic Pipeline (TAP AG) would be of irreplaceable importance. On the other hand, the needs of Kosovo and FYROM for gas supply and fluctuations in gas consumption make building underground gas storage possibly nearby the TAP route unavoidable. In many countries underground gas storages are built up in depleted sandstone, carbonate oil fields and in salt diapires. Albanian is rich in depleted sandstone and carbonate oil fields and salt diapirs. Investigations have been here made to find the most appropriate location for gas storage. Results reported that the Upper Miocene depleted sandstone gas fields in Divjaka and Povelça, and the Dumre evaporitic deposits diapir of the Upper Triassic age are the most appropriate locations. The later results as best target alternative for the very underground gas storage.

2. MATERIALS AND METHODS

Gas supply by interconnections pipelines was early estimated a strategic goal to secure rising energy demands after 2000 in Albania. Considering limited local reserves, desolated and depleted existing gas fields, EU Southern Gas Corridor projected after 2003 was supposed to impose new prospects. TAP route through Albania is not only a "gold" opportunity to dispose of low cost our energy supply, but a chance to offer the region nearby some possible targets of local gas fields for underground natural gas storage (Sota *et al*., 2000).

2.1. Divjaka gas field

The figure 3 and 4 depict the Divjaka gas field. The gas pool is accumulated into the anticline structure of Divjaka, which is an integral part of the Kraps-Ardenicë–Divjakë-Ballaj-Durr¸s anticline chain of the Durrës depression (Prenjasi *et al*., 2001). The Divjaka anticline is dissected by a thrust along its western flank and some secondary faults (back-thrusts) of up to 100-150 m vertical amplitude along its eastern flank (Figure 4). The latter have controlled the gas pools accumulations in the sandstone beds of the Messinian and Pliocene Age along the eastern flank of the anticline structure in question. The Messinian deposits from which are recovered considerable reserves (Kurti *et al*., 1999; Sota *et al*., 2000), are considered an interesting target for the gas storage in this exploited gas field. They underlay the Pliocene deposits and upper part consists of a clay package. The Divjaka sandstone gas-bearing suite is located in the lower part (Figures 4, 6).

The Divjaka suite is developed in the central part of the structure, whereas southward, northward and westward it changes lithologically into clays. It has a thickness of 150-170 m, where seventeen sandstone beds separated by clay intercalation are detected. The exploited sandstone beds number 1-6 and 8,

which locate in the central part of the field, have confirmed a high-gas-bearing potential as their permeability varies from 16.3 to 153.4 Md.

Fig.1. Trans Adriatic Pipeline alternative routes across southern Balkan countries (after ILF Consulting Engineers, 2009).

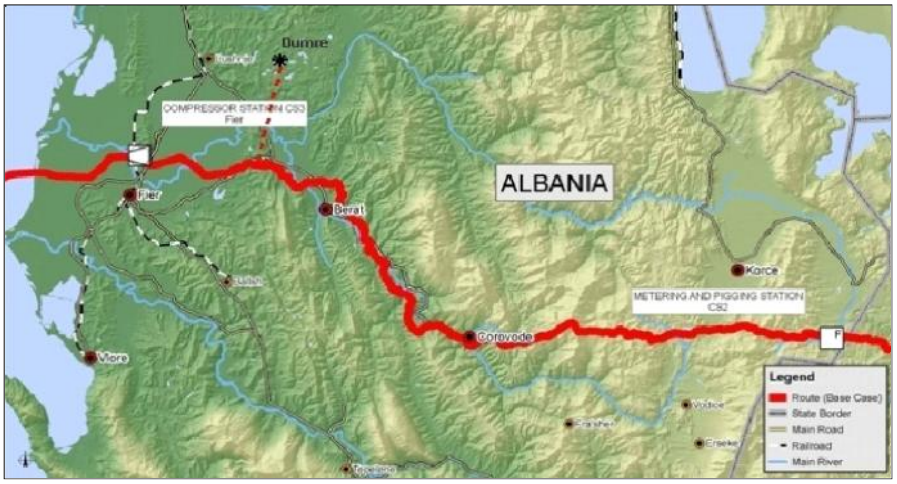

Fig. 2. Trans Adriatic Pipeline route across southern Albania *after ILF Consulting Engineers, 2009.*

Intended branch of the Trans Adriatic Pipeline to the Dumre diapir gas storage target.

Possible geological site for underground gas storage.

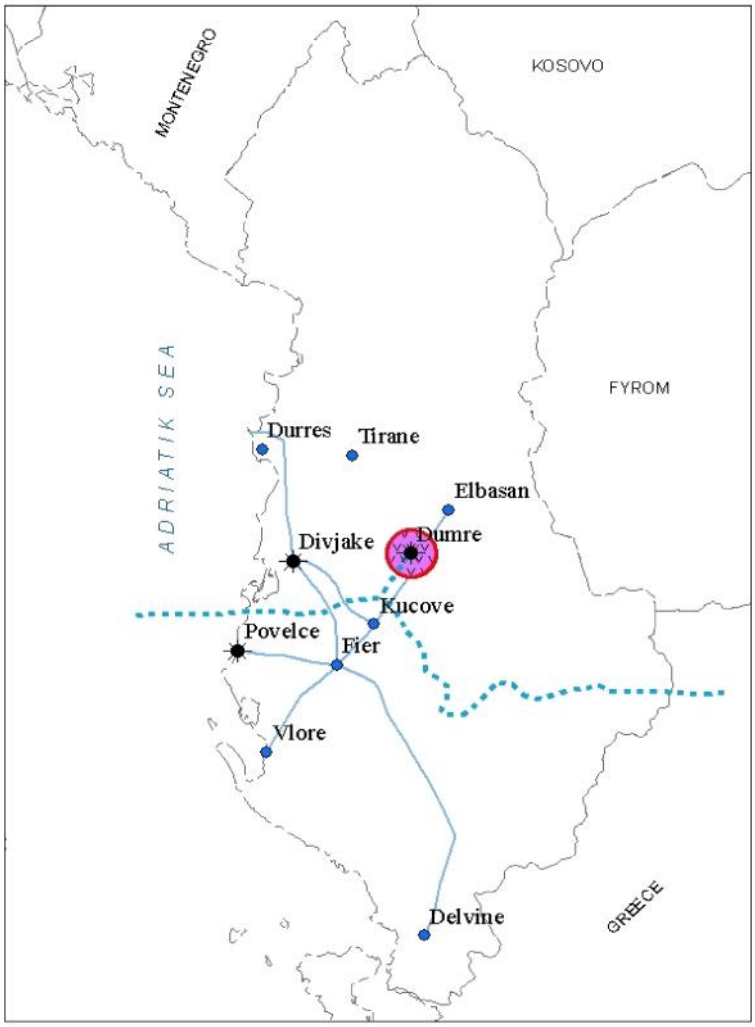

Fig. 3. Location of possible underground gas storage targets in Albania.
Outcrop of the Dumre diapir target.
Possible geological targets for underground gas storage.
..... Route of Trans Adriatic Pipeline (*after ILF Consulting Engineers, 2009)*, and its intended branch to the Dumre diapir gas storage target.
—— Existing gas pipeline network in Albania (*Ranxha, et al., 2000*).

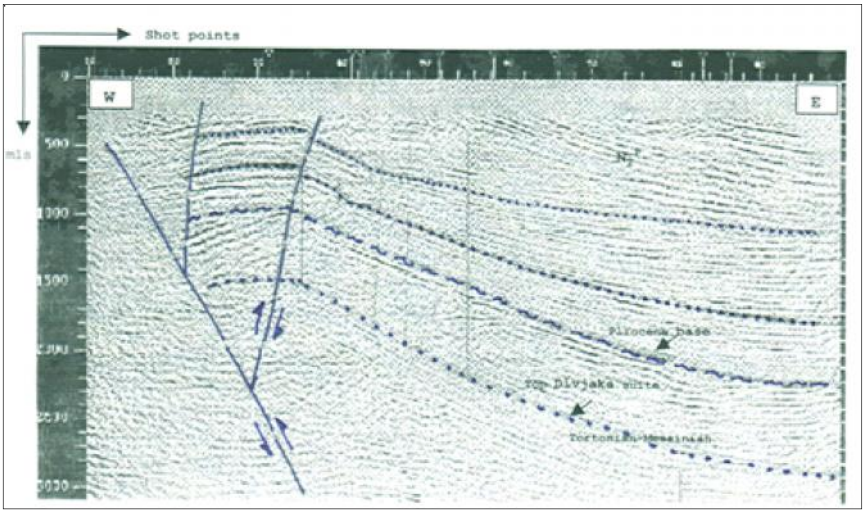

Fig. 4. Geoseismic profile across the Divjaka exploited gas field.
target (*Kurti, et al., 1999*; *Prenjasi, et al., 2001*). ..... Lithological boundary.

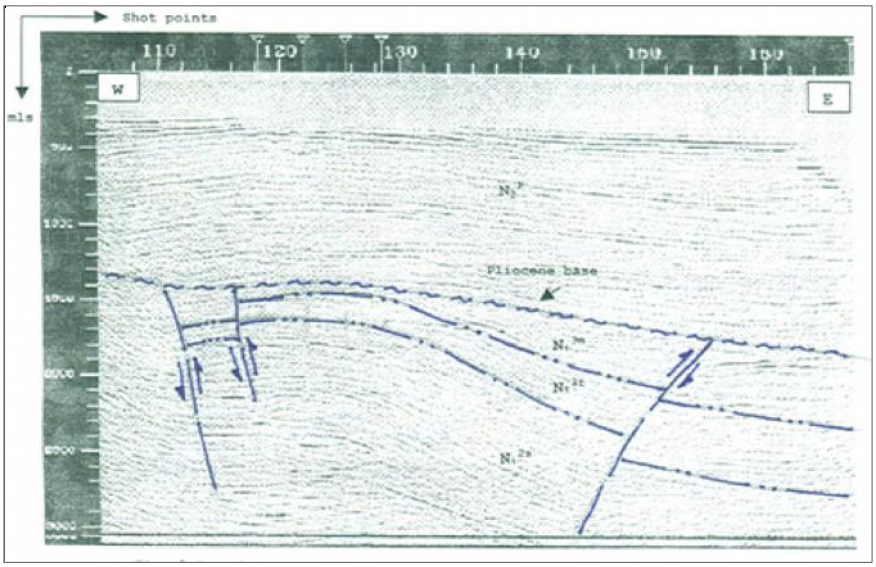

Fig. 5. Geoseismic profile across the Povelça exploited gas field target. (*Prenjasi, et al., 1997; Zajmi, et al., 1999*).
–.. –Geological boundary; $N_1^2{}_s$ Serravalian, $N_1^3{}_t$ Tortonian, $N_1^3{}_m$ Upper Miocene, N_{2p} Pliocene.

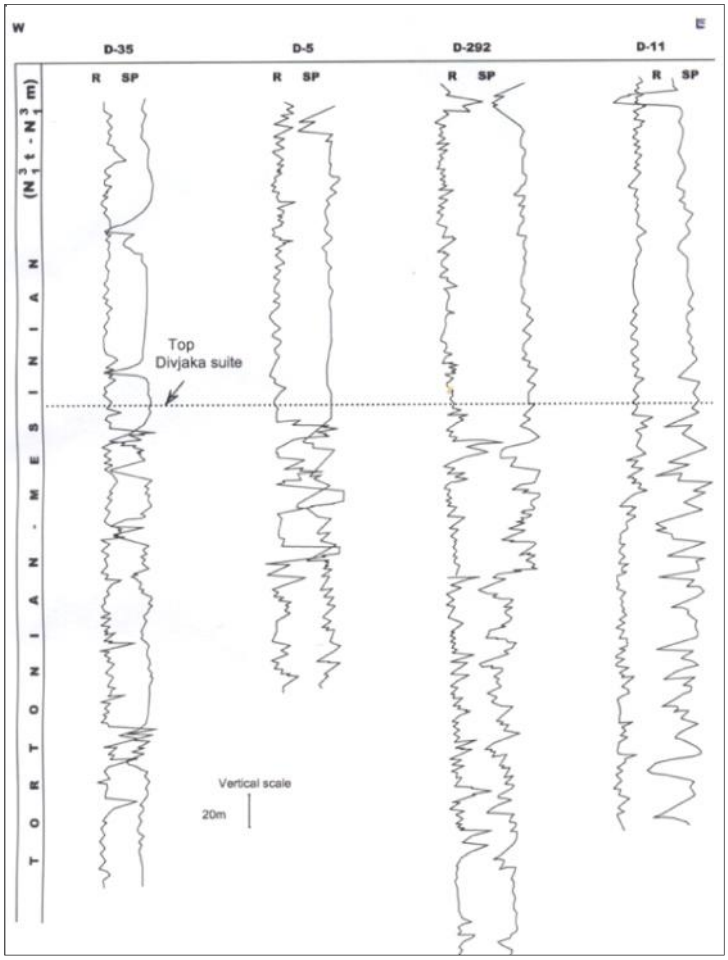

Fig. 6. Log correlation scheme of the Divjaka-35, 5, 292 and 11 drilled wells, across the Divjaka exploited gas field target (Kurti, *et al.,* 1999).
R- Electric resistance curve, SP- Spontaneous polarisation curve, lithological boundary.

Development regime of the Divjaka field is of gas extension drive. Gas pools depth is 2,600-3,400m. Initial bed pressure is 280-347atm. Initial bed pressure gradient is 1.15-1.24 atm/10m.Three main hydrodynamic zones are made out in the Messinian deposits of the Diviaka field (Kurti *et al.,* 1999). They are developed by 14 wells of 2,600-2,900m of depth. Kurti *et al.,* (1999) and Sota *et al.,* (2000) reported that the maximum permitted output of the three zones in all, at their initial stage of development has been some 1,500,000 Nm^3/day and after the 50% of their reserves recovered it is some 770,000 Nm^3/day.

2.2. Povelça gas field

The Povelça gas field is located in the western part of the Durr¸si depression, as an integral part of the structural chain of Poro-Povelç-Seman. This field represents a linear anticline with a considerable amplitude of its cross closure. It is dissected by a thrust along its western flank and a back-thrust along its eastern flank (Prenjasi, *et al.,* 1997; Zajmi, *et al.,* 1999), after figure 5. The geological column the Povelça gas field consists of the Pliocene deposits, which lies transgressively on the upper part of the Messinian ones. The latter lie conformably on the Tortonian deposits, which in the upper part (some 200-300m thickness) consist of turbidity faces of clays intercalated with lenticular sandstone, where some gas pools at different vertical levels are discovered. The sandstone beds' thickness varies from 5 to 18 m. Their porosity varies from 20 to 25% and permeability from 8 to 15 Md. Gas bearing reservoir is of structural-lithological type. Exploitation regime is of gas extension drive. Gas saturation is 55 -70%. The section has a high-pressure gradient of 1.4-1.6atm/10m. Initial bed pressure have resulted 300-500atm, while the remained one is 10-20atm.

Remained recoverable reserves of the Povelça gas pools, already exploited are some 50 million Nm^3 gas (Zajmi *et al.,* 1999). Progressive amount of the gas recovered from the field is about 270 million Nm^3. Initial outputs of the wells have been 30,000-90,000 Nm^3/day, while final ratio of gas recovery for the complete field is calculated about 90% of the initial recoverable reserves. Targets depth of the Povelça gas field ranges from 1,900 to 2,400m. In other words both exploited gas fields of Divjaka and Povelça have limited capacity for gas storage in their depleted sandstone beds. On the other hand these alternatives of gas storage bear the real risk of stored gas escape through possible well's casing or cement fractures that are undetectable and blocked easily.

2.3. Dumre evaporitic diapir

The figure 3 depicts the Dumre evaporitic diapir located nearby the north of the alternative route of Trans Adriatic Pipeline which crosses the southern Albania (Figures 1 and 2). It is the biggest evaporitic diapir occurred in Albanides with an ellipsoidal shape of approximately 12x18km in size, while its thickness penetrated by the Dumre-7 well is 6,119m (Figure 7). The Dumre evaporitic diapir is covered with numerous seismic profiles by which the whole evaporitic deposits are recorded as chaotic faces that contrast to the reflector horizons below and around its outside contour. Relied on the picked up samples and complete log data gained from several drilled wells, the lithological content of the geological section of the Dumre evaporitic diapir is a heterogeneous one.

Thus it is a real mixture comprising salt, gypsum, anhydrites, as well as

dolomite and limestone small blocks (Gjenerali *et al.*, 1971; Ranxha *et al.*, 2000; Sota *et al.*, 2000). It dates since Upper Triassic and can provide sure sealing condition for the natural gas storage. On the other hand the large sizes and thickness of the Dumre evaporitic diapir can provide unlimited storage capacity. Consequently, in this diapir opening several underground gas storages is possible. Once opened and put into function, gas supply for Albania and some other Western Balkan countries such as Kosovo and FYROM occurs.

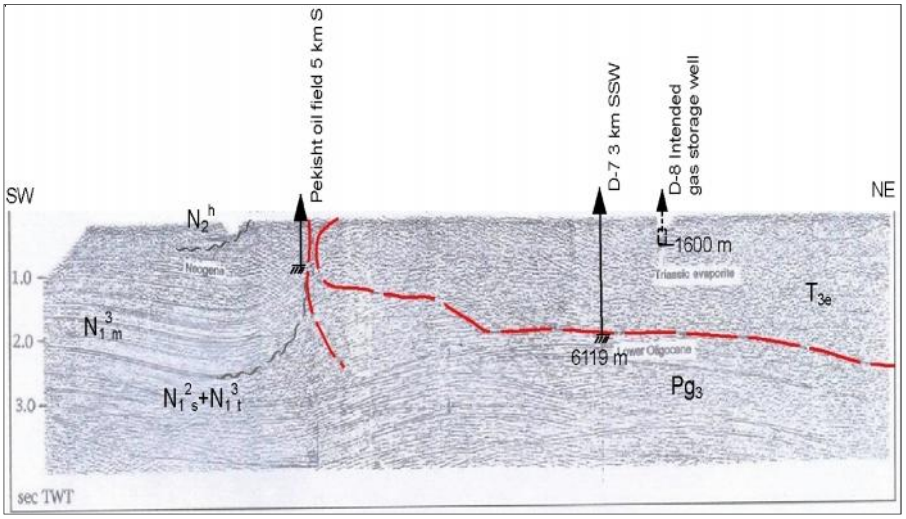

Fig.7. Geoseismic profile across the gas storage target of the Upper Triassic evaporitic deposits in the Dumre diapir.D-7 drilled well, N_2^h Lower Pliocene, $N_1^3{}_m$ Upper Miocene, $N_1^2{}_s + N_1^3{}_t$ Serravallian+Tortonian, Pg_3 Oligocene, T_{3ev} Upper Triassic (evaporate rocks).

3. RESULTS

The geologic and geoseismic data here reported lay the floor to debates and discussions. The project will be implemented in the beginning of 2015. The table 1 reports the current situation of natural gas field. No gas field was discovered in 2008 and investing in depleted gas fields was considered inadequate. So, they could be exposes as possible targets for underground gas storage in connection to TAP route expectances for energy supply.

Table 1. Gas Natural reserves on 01.01.2008

no.	GAS FIELDS	INITIAL PROVEN RESERVES (Nm3)	RESERVES till 01.01.2008 (Nm3)	Percentage to INITIAL PROVEN %	EXTRACTIVE RESERVES remains on 01.01.2008 (Nm3)
1	Divjakë	65,053,356	62,618,308	96.26	2,435,048
2	Ballaj Kryevidh	164,615,399	159,234,542	96.73	5,380,857
3	Povelça	128,557,771	119,466,292	92.93	9,091,479
4	Panaja	49,807,425	48,932,490	98.24	74,935
	TOTALLY	408,033,951	390,251,632	95.64	17,782,319

4. CONCLUSIONS

Many geological-geophysical integrated studies report that the exploited gas fields of Divjaka and Povelça and the evaporitic diapire of the Dumre area are appropriate locations for natural gas storage. The latter is the most appropriate location for underground gas storage due to its sure seal capability and unlimited storage capacity. The salt can be solution mined or leached out from the domal structure or strata into a desired storage shape and volume by a solution mining process. Fresh or low-salinity water is pumped down into the salt formation through a borehole (leaching string) and waste brine is returned through the withdrawal/production string to progressively dissolve the salt in a controlled manner. Salt can be used in road maintenance practices.

Located in the north of the Trans Adriatic Pipeline alternative route, the gas storage in the Dumre diapir can play a key role in the connection with the Albanian gas pipe network. Consequently, gas supply in some western Balkan countries like FYROM, Kosovo, Montenegro, etc. would be possible. Once the Trans Adriatic Pipeline alternative route starts erection across Albania, evaluating consumers needs would be unavoidable.

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COMPARATIVE CONSIDERATIONS ON THE RESPONSE OF SOME WHEAT VARIETIES ON LATE PLANTING

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ABSTRACT

Climate models predict an increase in the frequency and magnitude of rainy periods in the Albanian territory that are likely to occur during autumn months. Consequently, the planting process of wheat culture in the western part of the country is threatened. In addition to yield indicators, the present paper investigates on physiological and morphological characteristics of crops in three wheat varieties sown in November and January to estimate their reaction against late planting. Results report that the crops of STF4 and DxM varieties have a better response to late planting as compared to LB7 variety. Regarding the adaption of varieties to late planting, the key features to be improved have resulted to be photosynthetic system in LB7 variety and development speed in DxM and STF4 varieties.
***Keywords*:** wheat, heavy rainfall, climate change, photosynthetic pigments, yield

1. INTRODUCTION

Wheat is an important agricultural plant greatly linked with a state's economy and security (Mike and Davies 1997). Due to its high energetic content, it is extensively utilized in the food and other light industries. Furthermore, nowadays its usage as a biofuel is being promoted as well to reduce the consumption of

fossil fuels for energy purposes (Mike and Davies 1997) and as a consequence to trap the emission of greenhouse gases in the atmosphere. Consequently, building resilience of this culture to new climatic conditions in the frame of climate change would affect key socio-economic sectors of the country.

A detailed interdisciplinary investigation on the impact of climate change on crop production would be relevant. This culture in the western part of Albania is planted generally in the midst of November (Malo and Sako 2008; Laska 2009). The precipitation intensity and consistency during this period is the highest of the year (Mustaqi 1986; Porja 2010). In addition, climate models predict an increase of rainy extreme events in the Albanian territory that are likely to occur during autumn months. Albania is also projected to be one of the most affected countries by the phenomenon of climate change as compared to the other East European and Central Asian countries (World Bank 2009).

Predicted climate change scenarios such that of April 2010 are likely to constrain the process of wheat plantings in the most part of Albania. The planting of wheat started only in the first days of January in almost all the western part of the country. Under such conditions, the successful adaption of yeild process to the new climate features is challenging (Jaupaj 2013). Here, resilience estimation of wheat varieties' against late planting would be of primary importance. Investigating the impact of late planting and future climate scenarios would be of irreplaceable importance for resilient wheat culture.

The present paper evaluates the reaction of three wheat varieties against late planting. Consequently, it aims at assessing the negative effects of late planting in each variety and drawing recommendations on the main issues in the field of wheat production such as climate change, provided definitions of risks, vulnerabilities, resilience and adaptive capacity, and reviewed conceptual frameworks for climate change-related vulnerability.

2. MATERIAL AND METHODS

Two varieties of bread wheat (LB7 and DxM) and one of durum wheat (STF4) have been planted in two different time periods consisting of normal and delayed planting where the first period is designated in mid-November 2011 and the second in the beginning of January 2012. This experiment has been carried out in Valias, 20 km far from Tirana one year after an extreme rainy season where vast arable lands were inundated and when the planting of wheat was merely carried out on the beginning of January in almost all the western part of the country.

The same varieties were planted in the beginning of December in Lushnja situated in the South-Western part of the country. Lushnja distric and Tirana district have the same climatic conditions (IHM 1982; Laska 2009). As the soil is

more drained in Lushnja, an earlier planting process is possible. The results of the experiment carried out in Lushnja are here reported for comparative purposes. The drawn recommendation relate to the experiment carried out in Valias.

Six thousand seeds of each variety have been planted in three replicate alleys in both experimental plots based on a complete randomized block design with three replications. The agronomic works in the three plots have been similar.

In the beginning of anthesis stages, 20 flag leaves have been collected randomly in each plots' alley, and analysed for their photosynthetic pigment concentration utilizing the destructive spectrophotometric approach (Lichtenthaler 1987). The collected leaves have been extracted with 85% acetone (Academic Press 1976; Kraja *et al*., 2000) and measured for the optic densities using a spectrophotometer type 4802H UV/VIS Double Beam, in E663nm, E644nm and E452.5nm wave lengths. Such a measurement is performed in four replicates. The calculation of the photosynthetic pigment content has been based on the equations of Rebelen (Hunt 1982; Shehu *et al*., 2004; Lichtenthaler 1987). The collected leaves have been analysed for their surface area as well, multiplying their length and width with the cereal coefficient [axbx0.75] (Stamo 1995). Finally, the kernels weight and their number per spike have been estimated at the end of vegetative period analyzing 30 plants per each crop, 10 individuals from each alley.

The results obtained from the later sown plants have been compared with the results obtained from the normal time sown plants.

At the same time, results obtained from the experiment carried out in Lushja are here reported for comparison purposes, as Lushnja and Tirana have the same climatic conditions (Laska 2009).

In the present investigation LSD post Hoc ANOVAs test and the student test here made to assess their statistical confirmation using the SPSS 17 software.

3. RESULTS

Figures 1-3 depict the results obtained from the three targeted varieties both in the late planted and normal time planted crops. Additionally, the statistical LSD test performed for each analyzed indicator and crop is in table 1 reported.

Results report that the flag leaves of LB7 crops planted in January suffered from a significantly reduced concentration of the photosynthetic pigments in the anthesis stage (fig.1/a). In real terms, the average values of the pigment concentration appear to have decreased by 30% as compared to concentration of the normal time planted crops. Additional statistical tests, LSD (table 1) and t-test confirmed the changes in average values of this indicator between the two groups of crops (late and normally planted).

The figure 1 (b) does not depict any change in the surface area of the flag

leaves (fig. 1/b). In addition, statistical analyses do not report any change in the leafy area (table 1).

Concerning the kernel-yield indicators, this variety has revealed a significant deterioration both in grain weight and number per spike (fig 1/c; fig.1/d; and table 1).

Quite the contrary, the late planting seems to have induced in David x Mec crops a sharp increase of the pigment concentration occurring in their flag leaves (fig. 2) confirmed by both statistical tests as well. Here, the pigment concentration of crops planted in January is 146mg/gr. as compared to 125 mg/g in those planted in November, i.e., a 17% more dense pigment in flag leaves. However, to our surprise, the leafy area has been significantly reduced in the late planted crops as confirmed by both LSD and student test (Table 1).

In terms of yield indicators, these plants have revealed lower average values in their kernels weight and number per spike. Nevertheless, the changes have not been verified by both tests (LSD & student).

Interestingly enough, the STF4 variety crops have shown a great similarity in their response to the delayed planting time as compared to the DXM crops. Their photosynthetic system in the flag leaves has increased by 10% the pigments concentration as compared to the plants sown in November (fig. 3), confirmed as well by the statistical tests (table 1). The flag leaf surface as well has been significantly reduced as confirmed by LSD and test too.

Additionally, there have not been significant changes, as far as yield indicators are concerned. Actually, unlike the DXM variety, average values inlate planted crops have revealed a lower number of kernels in the spike and high grain. However, it is worth noting that such changes have not been confirmed by any of the statistical tests.

4. DISCUSSIONS

Results report that the late planted crops of LB7 variety have undergone a significant reduction in both yield elements. Furthermore, such deterioration seems to have been caused mainly by the reduced concentration of photosynthetic pigments revealed in flag leaves of crops in their anthesis stage. Actually, it is a well-known fact that the photosynthetic pigments are responsible for the photons capture as well as for the conversion of their energy into crops' assimilates (Kongjika and Kongjika 2004; Acevedo *et al.*, 2002). Many authors have analyzed and confirmed the strong correlation between yield and pigment concentration in leaves (Babani and Jorgji 1994; Stamo 1995; 2000; Kraja *et al.*, 2000; Shehu *et al*., 2004) and many others have emphasized anthesis stage in wheat crops as the key phase where the pigment concentration has a strong impact on yield indicators (Zhang *et al.*, 2009).

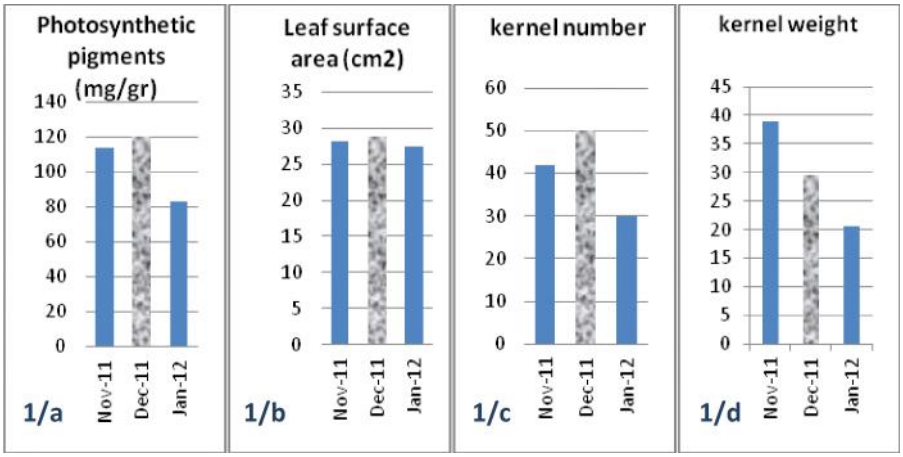

Fig. 1: Physiological and kernel-yield indicators revealed in crops of LB7 variety planted in November and January

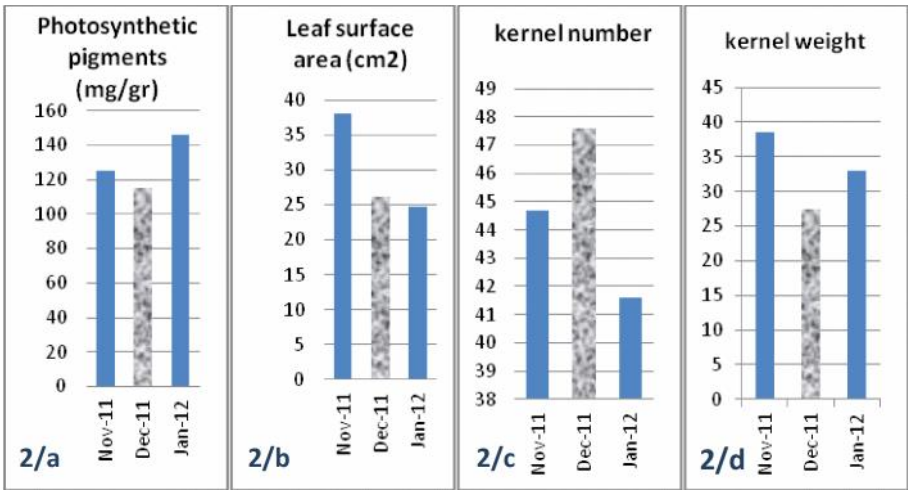

Fig. 2: Physiological and kernel-yield indicators revealed in crops of DxM variety planted in November and January

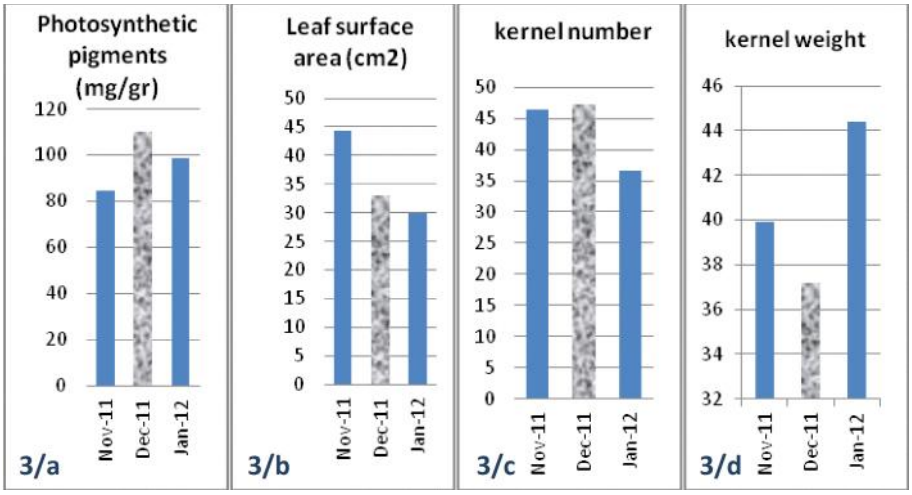

Fig. 3: Physiological and kernel-yield indicators revealed in crops of STF4 variety planted in November and January.

Table 1. LSD test on the changes in average values of analyzed indicators in crops planted in November and January

(I) Optimal Time		(J) Delayed time	Mean Difference (I-J)	Std. Error	Sig
November		December	-1.308	2.406	.589
		January	.000	2.610	1.000
Trait =Leaf surface					
November		December	-6396.295	4433.00	.183
		January	31848.533*	4433.00	.000
Trait=Photosynthetic pigments					
November		December	-8.45714	4.16809	.054
		January	12.34286*	4.16809	.007
Trait = Kernel number per spike					
November		December	9.24188*	2.77009	.003
		January	18.4720*	2.77009	.001
Trait=Kernel weight					

*The mean difference is significant at the 0.05 level.

(I) Optimal Time		(J) Delayed time	Mean Difference (I-J)	Std. Error	Sig
November		December	11.81*	2.39	.000
		January	13.28*	2.59	.000
Trait=Leaf surface					
November		December	9788.66*	515.55	.000
		January	-2.08E4	515.55	.000
Trait=Photosynthetic pigments					
November		December	-2.82	3.62	.444
		January	3.17	3.62	.389
Trait =Kernel number per spike					
November		December	11.16*	3.451	.003
		January	5.55	3.451	.119
Trait=Kernel weight					

*The mean difference is significant at the 0.05 level.

On the other hand, results report that the crops of the varieties DXM and STF4 were not able to develop sufficiently the leafy organs until the anthesis stage. Nevertheless, this abnormality appears to have been compensated to some extent by the sharp increase of pigments concentration in them because the plants revealed a good performance of kernel features (weight and number). In addition, it is apparent that the plants have not suffered by the abortion of kernels' creation, which is well-known to happen in the case of high temperature strikes during the anthesis stage (Acevedo *et al.*, 2002; Laska 2009; Anonymous 1984; Babani *et al.*, 1999).

As such, it is apparent that the crops of varieties STF4 and DxM have a better response to the late planting as compared to the LB7 variety. Actually, the robustness of the durum wheat, STF4 variety, to the abiotic stresses is comprehensible since many authors have affirmed the better resistance and resilience of durum wheat varieties toward a wide variety of stresses as than the soft wheat varieties (Stamo 1995). Meanwhile, as far as soft varieties are concerned, DxM is much more resilient to late planting than the LB7 var., at least regarding the analyzed features.

5. CONCLUSIONS

The conclusions drawn are as following: i) crops of STF4 and DxM varieties have a better response to late planting than the LB7 variety and, ii) the response of LB7 crops to the delay of planting process was a lower performance of the photosynthetic system with a decreased concentration of the pigment occurring in their flag leaves. The DxM and STF4 crops on the other hand have revealed a lower surface area of the flag leaves.

6. RECOMMENDATIONS

In the present investigation the following recommendations are drawn: i) the DxM variety is highly recommended to be planted in forced late panting events, ii) the photosynthetic system and pigment concentration regarding LB7 variety; the speed of development regarding DxM and STF4 varieties are crucial for the adaption of varieties to the late planting events, iii) further investigations are required with regard to resilience of the above-mentioned varieties such as the germination vigor of seeds, number of tillers and plant height, and detailed analyses of their photosynthetic system, assimilates distribution in plants, to name a few. Additionally, other varieties are needed to be tested concerning this issue and, iv) further investigations with regard to the impact that the forecasted climate change on crops especially cereals which are considered as key elements to human wellness.

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COMPARISON OF THE LEVEL OF SIMILARITY AMONG GRAPEVINE CULTIVARS OF KOSOVO BASED ON MORPHOMETRIC AND MOLECULAR DATA

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ABSTRACT

In the present paper, the grapevine cultivars Vranc (Vranac), Prokup, Rrush Keci, Rrush Melik, Thanz i Kuq and Thanz i Zi from three areas of Kosovo (Rahovec, Gjakove and Prizren) are investigated based on molecular and morphometric characteristics. Recommendations of the International Plant Genetic Resources Institute (IPGRI), of Consultative Group on International Agricultural Research (CGIAR) were followed for the ampelographic analyses and the results reported 31 morphological and agronomical characteristics. The Ward's method for hierarchical clustering was applied for the statistical analysis and a dendrogram of similarity among the cultivars was produced via JMP platform. The same data were used to prepare a three-dimensional graphic, which elucidated further the variation of morphometric data from one cultivar to the other. Ten decamer Randomly Amplified Polymorphic DNA (RAPD) were used as molecular markers and the results helped to prepare the dendrogram of similarity via the soft NTSYS 2.1. The ampelography data and molecular markers data inform about the level of similarity among the six cultivars. In addition, they report correctly on the level of phenotypic and genotypic variability. Meanwhile, both categories of data discriminate clearly the six cultivars, proving that none of them is homonymous of the

other. Four out six of cultivars have the same level of similarity. The cultivars Melik and Kec have a different clustering.
Keywords: grapewine cultivars, ampelography, RAPDs, genotypic similarity

1. INTRODUCTION

Kosovo is well known for the production of grapevines of high quality. However, in the last decades more attention has been drowned toward the enlargement of the production area. Detailed investigations on agronomical and molecular characteristics of the main cultivars have been carried out to provide accurate information about the genetic diversity of grapevines and to identify of native varieties. In the present paper the varieties investigated are Vranc (Vranac), Prokup, Rrush Keci, Rrush Melik, Thanz i Kuq and Thanz i Zi.

Ampelographic analyses were carried out to identify the morphological differences among grapevine cultivars of Albania and Kosovo. The analyses helps identify the names and classify grape cultivars through detailed analysis of the unique characteristics of the plant like morphology and different phases of development (Kryeziu, 2007; Kryeziu, 2011; Shundi and Osja, 2004; Susaj *et al*., 2003). Climatic conditions of the Dukagjini plane are investigated to determine the suitability for cultivation of grapevine (Koronica *et al*, 2005; Cena, 2005). Climate conditions expressed through the bioclimatic index (BCI) are suitable for the grape growth and the production of wine, even though the quantity of nutritive substances (nitrogen, phosphorous, potassium) is not high (Gashi *et al*., 2005). Randomly Amplified Polymorphic DNA (RAPDs) is in the present investigation used for the molecular evaluation of the cultivars of Kosovo and the results are here reported for the first time. RAPDs markers are generated by using short, random primers (9-12 nucleotides long) for the PCR amplification of genomic DNA. The PCR products show many bands, some of which may be polymorphic and can be scored as molecular markers in segregating populations (Gilmartin and Bowler 2002). Polymorphisms between two DNA samples occur whenever differences exist at the priming sites leading to polymorphisms of presence/absence of bands, or when insertions/deletions in the intervening sequences happen, leading to polymorphisms in the length of amplified fragments.

Currently, in different countries, different molecular markers such as RFLP, RAPDs, and SCARs. RAPDs and STMS have been used successfully to assess the genetic relatedness of grape cultivars (Stavrakakis *et al*., 1997; Gonzales-Andres *et al*., 2007; Lefort *et al*., 2002; Aras *et al*., 2005; This *et al*., 1997; Ercisli *et al*., 2008). Different investigations carried out in Albania provide inforamtion about the use of molecular markers of type RAPDs for the

discrimination of the genetic variability at population level for different plant species of economical importance such as olive, pomegranade, aromatic-medicinal plants, etc. (Bacu *et al*., 2005; 2009; 2013; Bacu and Thomaj 2010; Daskalova *et al.*, 2011; Ladoukakis *et al.*, 2004; Trojani and Bacu, 2008). However, microsatellites were seen as a promising category of molecular markers due to the problems with the reproducibility of bands. The latter are repeated in simple sequence motifs, which represent a great source of genetic variation (Bowers *et al*., 1996; Ladoukakis *et al*., 2004; Gonzales-Andres *et al*., 2007; Sefc *et al*., 1999, 2000, 2011; Lefort *et al*., 2002; Martin *et al*., 2003; Hizarci *et al*., 2012). So far, *Vitis* SSR primers have been developed by many groups (Bowers *et al*., 1996; Sefc *et al*., 1999), and their usefulness has been assessed in grapevine cultivars in Australia, California and Central Europe. Microsatellites are codominant markers that can interpret both alleles of a heterozygous diploid organism (Lefort *et al*., 2002). As a result they can also reveal chimerism or different levels of ploidy.

2. MATERIALS AND METHODS

In the present paper the cultivars Vranc (Vranac), Prokup, Rrush Keci, Rrush Melik, Thanz i Kuq and Thanz i Zi collected in Rahovec, Gjakovë and Prizren in Kosovo are investigated.

The ampelography analyses were carried out following the recommendations of the International Plant Genetic Resources Institute (IPGRI), of Consultative Group on International Agricultural Research (CGIAR) and the results are in table 1 reported.

The statistical analysis of the data was carried out via the JMP platform, and a dendrogram of similarity among the cultivars was created. The same data were used to prepare a three-dimensional graphic, which elucidated further the variation of morphometric data from one cultivar to the other, for each growing area.

The molecular data were based on the RAPDs (Randomly Amplified Polymorphic DNA) markers verified on the above cultivars. The decameric primers used were: OPB8, OPB9, OPB11, OPB12, OPB19, OPB20, P2, P6, tr5, OPC15 from Operon.

The genomic DNA was extracted from ten parallel plants for each cultivar, from fresh leaves, based on CTAB method modified.

The PCR reaction conditions were: 1UTaq polimerase, 1X bufer PCR, 1,4 µl $MgCl_2$ 25mM, 100µM from each deoxynucleotide, 100pmole primer, 25ng template ADN. The respective volumes were calculated for a total volume of 10µl.

Cycling conditions were: 94ºC for 4min, 36 times the following conditions: 94ºC for 1min, 94ºC for 10 s, 32ºC for 1 min, 72ºC for 1 min, 72ºC for 5 min.

Electrophoresis of the PCR products was conducted in 1,5% agarose gels in

1x TAE-Tris Acetate EDTA. The markers used to estimate the fragments dimensions were 20bp, 100bp and 1kbp and photos were taken under UV light.

The statistical analysis of the molecular results was initiated through the preparation of a binary matrix, which was further processed via the software NTSYS, 2.1 to create a dendrogram of genetic similarity among the six cultivars.

Finally, both dendrogramma were compared to each other based on the level of similarity they display among cultivars.

3. RESULTS

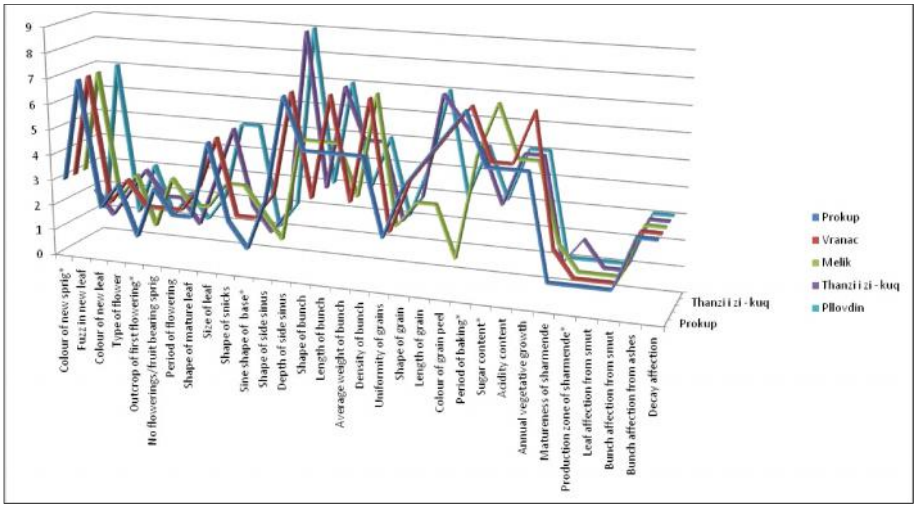
First, the present paper aims at preparing the table with the ampelographic data on the six cultivars of Kosovo (Rahovec, Prizren, Gjakovë). Table 1 reports on the characteristics measured according to the IPGRI descriptor.

Table 1. Ampelographic data of the grapevine cultivars Prokup, Vranc (Vranac), Kec, Melik, Thanz i Zi and Thanz i Kuq, cultivated in Kosovo based on ampelographic data, 31 parameters according to the descriptor of IPGRI of CGIAR (Consultative Group on International Agricultural Research).

No	**Attribute estimated**	**Code**	**Levels**	**Estimation: from left to right order 1. Prokup, 2.Vranac, 3. Kec, 4. Melik, 5. Thanz i Kuq-i Zi**
1	**Colour of new spring**	7	1,2,3	3,3,1,3,2
2	Fuzz in new leaf	4	0,1,3,5,7,9	7,7,7,7,1
3	Colour of new leaf	51	1,2,3,4,7	2,2,1,2,2
4	Type of flower	151	1,2,3,4,5	3,3,3,3,3
5	**Outcrop of first flowering**	152	1,2,3	1,2,1,1,2
6	No flowering/fruit bearing spring	153	1,2,3,4	3,2,2,3,2
7	Period of flowering	302	1,2,3,4	2,2,1,2,1
8	Shape of mature leaf	67	1,2,3,4,5	2,3,2,2,3
9	Size of leaf	605	1,3,5,7,9	5,5,5,2,5
10	Shape of snicks	76	1,2,3,4,5	2,2,5,3,2
11	**Sine shape of base**	79	1,2,3,..9	1,2,1,2,1

12	Shape of side sinus	82	1,2,3,4	3,3,2,1,2
13	Depth of side sinus	u-30	1,3,5,7,9	7,7,9,5,9
14	Shape of bunch	202	1,2,3,4,5	5,3,3,5,3
15	Length of bunch	203	1,3,5,7,9	5,7,7,5,7
16	Average weight of bunch	502	1,3,5,7,9	5,3,3,3,5
17	Density of bunch	204	1,3,5,7,9	5,7,5,7,5
18	Uniformity of grains	222	1,2	2,2,2,2,2
19	Shape of grain	223	1,2,3…9	4,4,4,3,3
20	Length of grain	221	1,3,5,7,9	5,5,7,3,7
21	Colour of grain peel	225	1,2,3…6	6,6,3,1,6
22	**Period of baking**	304	1,3,5,7,9	7,7,5,5,5
23	**Sugar content**	505	1,3,5,7,9	5,5,3,7,3
24	Acidity content	506	1,3,5,7,9	5,5,5,5,5
25	Annual vegetative growth	351	1,3,5,7,9	5,7,5,5,5
26	Matureness of sharmende	355	1,2,3,4	1,2,1,2,1
27	**Production zone of sharmende**	358	1,2,3	1,1,1,1,2
28	Leaf affection from smut	452	1,3,5,7,9	1,1,1,1,1
29	Bunch affection from ashes	453	1,3,5,7,9	1,1,1,1,1,
30	Bunch affection from smut	456	3,5,7	3,3,3,3,3
31	Decay affection	459	3,5,7	3,3,3,3,3

Second, the present paper aims at investigating the variation of the ampelographic characteristics among cultivars using a three-dimensional graphic which considers the 31 categories of IPGRI descriptor (Graphic 1). Once the investigation of the variation of the ampelographic characteristics among cultivars using a three-dimensional graphic is carried out, a dendrogram of similarity among cultivars, based on the same data is prepared (Fig. 1). In the present paper the Ward's method for hierarchical clustering was applied to investigate the similarity (Ward, 1963). The distance between the clusters was calculated using the squared Euclidean distance. The JMP platform (JMP) was used to calculate similarities automatically, and to generate the classifying dendrogram.



Graphic 1. Variability of the ampelographic characteristics among grapevine cultivars of Kosovo based on ampelographic data, 31 parameters according to the descriptor of IPGRI of CGIAR (Consultative Group on International Agricultural Research).

Graphic 1 illustrates the variability of the ampelographic data showing that the six cultivars are different, even though values are close to each-other. Basing on morphometric parameters, table 1 and Graphic 1 show that cultivars Thanz i Kuq and Thanz i Zi are considered as identical. The morphometric parameters reported in this table are the mean values for the Northern and Southern areas of Kosovo. However, most of the parameters for these two cultivars grown in different regions of Kosovo are different.

In order to establish a dendrogram of relatedness among the six cultivars, the 31st morphometric data were used, and displayed the Fig. 1. In this dendrogram, the grape cultivars are clustered in two, sharing a similarity, which confirms that none of them is homonymous.

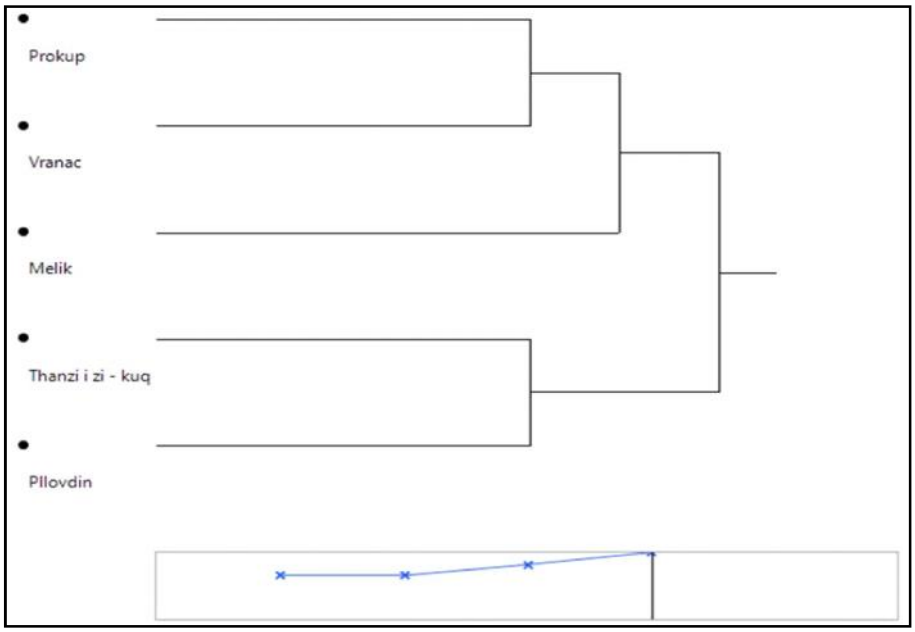


Figure 1. Dendrogram of similarity among grapevine cultivars of Kosovo, based on ampelographic data, 31 parameters according to the descriptor of IPGRI of CGIAR (Consultativ Group on International Agricultural Research).

Used to construct the dendrogram in Fig. 1, the Distance Matrix among the six cultivars based on morphometric data is here reported.

Name	Prokup	Vranac	Melik	Thanzi i zi - kuq	Kec
Prokup	0	5.916079783	6.348638943	6.605372993	6.535022308
Vranac	5.916079783	0	6.974134338	6.730350589	7.144217935
Melik	6.348638943	6.974134338	0	8.570879671	7.959004548
Thanzi i zi - kuq	6.605372993	6.730350589	8.570879671	0	6.04777349
Kec	6.535022308	7.144217935	7.959004548	6.04777349	0

It describes the level of similarity among cultivars numerically and provides a better indication on the clustering proximity.

Third, the present paper aims at providing information about the RAPDs based discrimination among the six cultivars, and preparing a dendrogram of similarity according to the RAPDs binary data, using the UPGMA cluster analysis method of the program NTSYS 2.1 (Fig. 2).

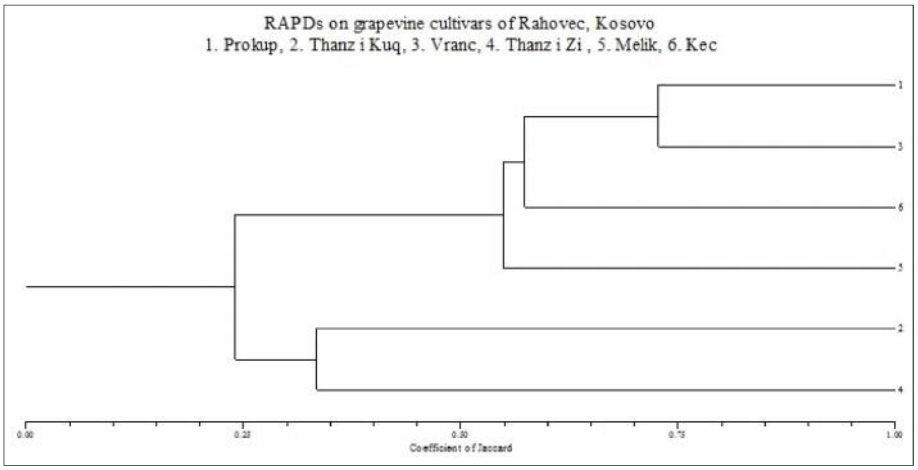


Figure 2. Dendrogram of similarity among six cultivars named from 1-6, according to the RAPDs binary data using the UPGMA cluster analysis method of program NTSYS 2.1.

In the figure 2 the cultivars are grouped in two clusters which share 25% similarity. The first cluster contains the cultivars Thanz i Zi and Thanz i Kuq, and the second contains the rest of cultivars. Reported in the dendrogram of similarity based on morphometric data (Fig. 1), and the one based on molecular data (Fig. 2), the genetic similarities among cultivars are comparable. In both cases, the cultivars Thanz i Kuq and Thanz i Zi are grouped together (even though the morphometric data consider them as identical, while the molecular data discriminate clearly, but cluster at the same group). Prokup and Vranc (Vranac) cultivars in both categories of data are grouped together. Melik and Kec cultivars from the morphometric data result in different clusters. Kec cultivars and Thanz cultivars are grouped together, while the molecular dendrogram considers cultivar Kec as member of the first cluster, distant from them. However, the coefficient of similarity in both cases differs by 2.5% in a scale from 0 to 1, which means that the cultivars named Kec and Melik are distant from the rest of the cultivars, they share with cultivars Thanz 25% of similarity, and with each-other 45-50% of similarity.

4. CONCLUSIONS

Results of both morphometric and molecular analysis of six grape cultivars of Kosovo prove that the six cultivars named Thanz i Kuq, Thanz i Zi, Melik, Kec (Pllovdin), Prokup and Vranc (Vranac) are not homonymous.

Clustering of cultivars based on both categories of data is comparable, and divides them in two main clusters, which share 25% similarity.

Within clusters, cultivars Prokup and Vranc (Vranac) group together sharing a 75% similarity; cultivars Thanz i Kuq and Thanz i Zi share 35% similarity (in molecular level).

For cultivars Melik and Kec, the clustering based on morphometric data differs from that based on molecular data. However, in both cases they appear distinct from each-other and from the rest of cultivars.

Molecular data of the aforementioned six cultivars of Kosovo are here reported for the first time.

Investigations involving other cultivars must further to elucidate their genetic relatedness, and find out native cultivars among them.

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EVALUATION OF BLOOD DONOR DEFERRAL CAUSES

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ABSTRACT

Currently, causes of donor deferral for both male and female have been retrospectively evaluated. The data were collected at the National Blood Transfusion Center (ANBTC) and outdoor camps in Tirana, Albania from January 2011 to January 2013. In the present study, 12,306 blood donors are involved. Each donor was selected by a medical officer based on detailed medical history and brief physical examination with regard to haemoglobin, blood pressure, temperature, and pulse regularity and rate. Detailed information about the donor deferral including the cause of deferral was recorded in the deferral register. Relative proportions to detect the rate and reason for donor deferral have been found. 1449 out of 12,306 voluntary non-remunerated donations were deferrals (11.7%). 1127 (77.8%) were temporary deferrals and 322 (22.2%) permanent deferrals. Investigations on temporary deferrals revealed 698 (48.17%) anemia, blood pressure or pulse 350 (24.2%), 81 (5.5%) other medical conditions. In addition, it revealed 92 (6.37%) donors deferred for high risk behaviour/exposure, 228 (15.73%) for chronic diseases and 65 (4.48%) for other pathologies including history of jaundice. Currently, in Albania all the voluntary non-remunerated donors are collected at mobile session, and even if to temporary excluded donors is given a date for next donation they never return to donate. None of the 1?127 voluntary non-remunerated donors temporary deferred from 2011 to 2013 and came back to donate.

Keywords*:* blood donor deferral, permanent, temporary

1. INTRODUCTION

Individuals disqualified from donating blood are known as “deferred” donors. The rate and reasons of deferral are different from one region to another and sometimes within the same region. Physical conditions and medical history determine the eligibility criteria of the donor. Careful donor selection is of crucial importance for both donor and recipient as infection risks could be prevented.

As the donors donate blood willingly, they have to be carefully deferred or rejected on scientific grounds. In addition, they have to be informed whether and when can return. Donor deferral rates should be closely monitored by the blood bank physician to ensure they are within a reasonably range-usually less than 12%.

Donors are either interviewed by a qualified staff member or they are allowed to complete the records themselves. Once completed, the records are reviewed by a specialist. Once reviewed, the outcome is communicated to the donor. The interview and physical examination should be performed in a manner that ensures adequate auditory and visual privacy, allows time for any necessary discussion or explanation. Answers to questions recorded with "yes" or "no" with details explaining yes answers added as indicated. Results of all tests have been recorded in a special register.

Voluntary blood donors are selected based on the records reported, haemoglobin values and medical examination (anamnesis and physical examination), following the standard operative procedures (EDQM, 2010). Stringent donor screening criteria are of irreplaceable importance as eligible donors are carefully selected. Consequently, both donors and recipients are saved.

There are many reasons that can lead to temporary or lasting rejection of blood donors.

A proper process of selecting a "safe" voluntary donor leads to safe transfusion (Newman, 2001). In the present study, most of voluntary non-remunerated donations are collected at mobile sessions, and most of them still are first-time donors. Therefore, if a donor is deferred from donation at mobile session, appropriate data collection and strategy would be very important for having back the donor as soon as he becomes eligible.

The present study aims at evaluating donor deferral causes in voluntary non-remunerated blood donors, in order to design a strategy for donor recall.

2. MATERIALS AND METHODS

Recently, a retrospective study with regard causes of donor deferral for both male and female has been carried out at the National Blood Transfusion Centre (ANBTC) and outdoor camps in Tirana, Albania from January 2011 to January 2013.

The present study involved 12 306 donors. The volume of blood collected was 350 ml or 450 ml depending on the weight of the donor: 350 ml was collected from donors who weighed 45-60 kg and 450 ml from donors who weighed above 60 kg (EDQM, 2010). Parameters taken into account for evaluation were age, gender, previous donations and reason for deferral.

Each donor was selected by a medical officer based on detailed medical history and brief physical examination with regard to haemoglobin, blood pressure, temperature, and pulse regularity and rate. Detailed information about donor deferral including the cause of deferral was recorded in the deferral register. Criteria laid down by the general director of Health Services of Albania (HSA) were strictly followed. Deferral by self was not considered, as it was difficult in our setup. The relative proportion to detect the rate and reason for donor deferral was found.

3. RESULTS

The demographic profile of the donors is in table 1 reported. In the present study 2306 blood donors are involved. Men constitute 7.89% (7654) of the deferred donors. Women constitute 18.1% (4652) of the deferred donors. Nevertheless, the deferral rate is higher in women. Temporary deferral was more common than permanent deferral. Temporary deferrals constitute 77.8 % of the deferred blood donors and permanent deferrals constitute 22.2% of the deferrals donors (Table 2).

Table 1. Demographic profile of the donors and deferral by gender

	Men	**Women**	**Total**
Number of donors	7654	4652	12306
Number deferred	604	845	1449
% deferred	7.89	18.1	11.7

Table 2. Frequency of permanent and temporary deferrals

	No. of deferrals	**% of total deferrals**	**% of deferrals of total registration**
Temporary	1127	77.8 %	9.15 %
Permanent	322	22.2 %	2.61 %
Total no. of deferrals	1449	100.0%	11.77 %

Donors are deferred for multiple reasons. Losses related to disease marker rates are well-established in our country. Donor losses for other reasons have not extensively been quantified.

The three most common reasons for deferral are: i) low haemoglobin levels, 5.67 % of the donors or 48.1% of the rejected donors, ii) hypotension and hypertension, 2.85% of the donors or 24.2% of the rejected donors and, iii) other medical conditions, 1.85% of the donors or 15.7% of the rejected donors. Other reasons for deferral are: i) high risk behaviour, 0.26% of the donors or

2.21% of the rejected donors, ii) high risk exposure, 0.49% of the donors or 4.16% of the rejected donors and, iii) travel and other reasons, 0.53 % of the donors or 4.5 % of the rejected donors. In the present study the unsuccessful phlebotomy is only 0.12%. (Table 3)

Table 3. Causes of reasons for rejecting blood donors with their relative proportions

Causes	No of volunteers	Frequency of rejection %	Deferral reasons%
Low Hb	698	5.67	48.17
Low or High blood pressure	351	2.85	24.22
Antibiotics	228	1.85	15.73
Risk behaviour	32	0.26	2.21
Risk exposure	60	0.49	4.16
Other pathologies	65	0.53	4.48
Miscollection	15	0.12	1.03
Total of deferral	**1449**	**11.77**	**100.00 %**
Total of volunteers	**12306**		

Reasons for rejecting the blood donors and their relative proportions are shown in the table 3. The table reports that the leading reason for rejecting the female donors are low Hb levels due to a high prevalence of anemia in the female population (562/698), the leading reason for rejecting the female donors are low Hb levels. High blood pressure is the leading reason for rejecting the male donors (268 /351).

4. DISCUSSION

As the donors donate blood willingly, they have to be carefully deferred or rejected on scientific grounds. There are definite advantages of eliminating donors with possible risk of disease because despite the availability of sensitive screening tests to detect HIV infection, blood donors can be infected but test negative if they have been infected for a period of 6 weeks or less (Custer *et al.*, 2004). Deferring donors also protects the donors from possible adverse reactions and avoid consequent negative impact on the donor motivation.

Deferral rate is different from one region to another and sometimes within the same region (Bahadur *et al.*, 2009; Rabeya *et al.*, 2008; Arslan, 2007). In the present study, the overall deferral rate is about 12%. Well-organized blood monitoring programme with quality systems is essential for the provision of safe blood supplies that are sufficient to meet the transfusion requirements of patients at all times and in all parts of the country, including remote regions.

This is of primary concern for the Albanian Blood Service (ABS). The implementation of the quality control program started in Albania in 2009. The data are here reported for the first time. In the present study, the unsuccessful phlebotomy is only 0.12%. Farrales *et al.,* (1997) reported a higher rate of 0.5% and Custer *et al.*, (2004) reported miscollection leading to 3.8% of 1001,141 collections.

Donor deferral (11.7%) in the present study reported is approximate to various studies. Zou *et al*., (2008) reported a deferral rate of 12.8% in their six years study of American Red Cross blood service and Custer *et al.,* (2004) showed a deferral rate of 13.6%. Lawson and Salmi (1999**)** reported that 10.8% of donor's volunteers were deferred.

Many research papers report that anemia is the common cause for deferral (Farrales *et al,* 1997; Zou *et al*., 2008). In Albania, required haemoglobin is 125 g/ml both for male and female, for blood donation. In Canada, 2% of all blood donors do not meet the minimum haemoglobin level required, whereas in developing countries the number is more as pointed by this study (more than 7%).

In the present study, anemia is the most common cause for deferral. Halperin *et al*., (1998) reported almost the same reasons for deferral. He stated that the low haemoglobin level was the leading cause for deferral in 46% of the temporary donors.

Anemia can be cured if proper treatment of these donors is undertaken with follow up. A proper track for follow up of temporarily deferred donors regarding their management should be made in the blood bank so that these donors can be recruited back in donors' pools.

6.37% or (92) of the donors deferred for high risk behaviour/exposure are under permanent deferrals. 15.73% (228) of the donors are deferred for chronic diseases and 4.48% (65) for other pathologies including history of jaundice.

Having a tattoo has been associated with serological evidence of hepatitis B and C viruses, as well as HIV infection and syphilis, all these are known to be transmissible by blood transfusion. These associations are of higher magnitude for individuals having two or more tattoos unprofessionally applied and are common among drug addicts and prisoners. (Nishioka *et al.,* 2002; Choudhury and Tetali 2008). In Albania, tattooing is not common and constitutes about 2% of deferrals, including high risk behaviour.

5. CONCLUSIONS

Anemia is the most common cause for temporary deferral in female donors. There was a statistically significant difference among anemic donors as the majority of them were females (562 out of 698) were females, reflecting the condition of the general population in our country.

Miscollection does not seem to be a problem, in many settings. In the present study the miscollection rate is low (only 0.12 %). Here, a good technique for phlebotomy has been applied by well-trained phlebotomists.

As blood insufficiency rate is low in Albania, a strategy to recall all the temporary deferred donors has been designed in partnership with the organizations involved in the area.

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THE CORRELATION BETWEEN LIPID PROFILE IN PREGNANCY AND HYPERTENSION IN PREGNANCY IN TIRANA REGION (ALBANIA)

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ABSTRACT

Pregnancy induced hypertension (PIH) represents a major obstetric problem in healthcare practice. The role of lipid metabolism in the development of PIH and preeclampsia is gaining increasing attention. The present paper aims at assessing the role of lipid profile in the aetio-pathogenesis of HIP and preeclampsia. The study involved 122 pregnant woman divided into 3 groups: pregnant hypertensive women (n=26); pregnant normotensive women (n=68); and non-pregnant normotensive women (n=28) [control group]. All of them did not have previous history of chronic hypertension, renal disease, dyslipidemia or diabetes mellitus. Serum triglyceride, total cholesterol, LDL Cholesterol and HDL cholesterol levels were measured. The results showed that mean serum levels of triglyceride, total cholesterol and LDL cholesterol were significantly higher among PIH women compared to pregnant normotensive women and control group whereas HDL cholesterol was significantly higher among controls. Total cholesterol showed a statistically significant correlation with gestational age ($r= 0.550$, $p<0.001$). Diastolic blood pressure showed moderate negative correlation with HDL ($r=0.494$) which was statistically significant ($p<0.001$). In conclusion women with PIH showed mild hypertriglyceridemia and a significantly deteriorated lipid profile compared to pregnant normotensive and healthy non-pregnant women. Further studies need to be undertaken in order to ascertain the temporality of associations between lipid profile and PIH.

Keywords: Pregnancy Induced Hypertension (PIH), preeclampsia, triglycerides, LDL cholesterol, HDL cholesterol

1. INTRODUCTION

Pregnancy induced hypertension continues to be a major obstetric problem in present days health care practice. It presents a great medical dilemma because it affects not only maternal health but also puts fetal development at risk.

Worldwide, the hypertensive disorders are common and responsible for 12% of maternal mortality during pregnancy and the puerperium. Pre-eclampsia is the leading cause of maternal mortality in developed countries and is associated with a fivefold increase in prenatal mortality. The major cause of fetal compromise in preeclampsia is the reduced uteroplacental perfusion (Bellany *et al*., 2007; Slomon *et al*., 2001).

Dyslipidemia is common in pre-eclampsia and via oxidation of susceptible lipids may contribute to endothelial activation. Many investigations provided information about the relationship between essential hypertension and serum lipids (Asaolu and Asaolu 2010; Jayanta *et al.,* 2006). It has been found that abnormal lipid profiles are strongly related with atherosclerotic cardiovascular diseases and causes endothelial dysfunctions. The most important feature of pregnancy induced hypertension is hypertension via vasospasm in kidneys, uterus, placenta and brain. Primary source of prostacyclin and thromboxane are endothelial prostacyclin and thromboxane, which are endothelial and thromboxane cells respectively. In normal pregnant women, endothelial prostacyclin reaches levels up to 8-10 times higher than a pregnant woman; while the rising is even higher in pre-eclamptic women, due to the thromboxane levels that reach highest values in preeclamptic women. Endothelial cell destruction is caused because thromboxane prostacyclin level is raised leading to vasospasm. Increasing lipid synthesis causes rise in thromboxane prostacyclin rate and plays a role in the pathogenesis of pregnancy induced hypertension. Abnormal lipid profiles may become an important marker for pregnancy toxemia. The present investigation aimed at evaluating the role of lipid profiles in aetio-pathogenesis of pregnancy induced hypertension.

2. MATERIALS AND METHODS

In the present investigation 128 pregnant women ranging from 24 to 36 years divided into 3 groups: pregnant hypertensive women (n=26); pregnant normotensive women (n=68); and non-pregnant normotensive women (n=28) [control group]. It was carried out at the Department of Obstetrics and Gynecology, University Hospital Koço Gliozheni, in Tirana, Albania between May and August 2014. Informed verbal consent was obtained from all the patients. During selection of the potential patients were collected a detailed health history and the individuals with a history of hypertension thyroid diseases, renal diseases, diabetes mellitus, and dyslipidemia were excluded from the investigation.

From all the groups, 8/10 ml blood samples were taken from antecubital vein after 12 hours of house fasting. The blood samples were centrifuged for 4 minutes at 4.000 rpm, and kept for 30 minutes at room temperature to separate

the serum fluids from red blood cells. Chemical analysis was conducted using a 721-2000 VMCS Spectrophotometer. Total cholesterol levels were measured by cholesterol esterase/oxidase method. Plasma was mixed with phosphotungstic acid in the presence of magnesium divalent ions, spun. HDL-cholesterol levels were measured in supernatant by the cholesterol esterase oxidase method. TG triglycerides were assayed by coupled enzymatic, using glycerol kinase. The LDL-cholesterol fraction was obtained by using Fried field formula, where TG concentration is less than 4.4 mmol/l.

$$LDL_{cholesterol} = Total\ cholesterol - \left(\frac{TG}{2.2 + HDL_{cholesterol}}\right)$$

Statistical analysis was done using SPSS version 17. Test of significance was analyzed by T-student test. Pearson method was applied to evaluate the correlation analysis. Results reported that the level of significance was considered at $p<0.001$.

3. RESULTS

Table 1 reports the demographic profile of the patients divided in non-pregnant, healthy pregnant and pre-eclampsia subjects. Across the groups, the mean age was 30, 35 and 29 years, respectively. Mean systolic and diastolic blood pressure were higher in women with preeclampsia (group 1), compared to the control group 2 and non-pregnant women (group 3). Mean gestational age in the pre-eclampsia and normal pregnancy groups were 33 and 26 weeks, respectively.

Lipid profiles in the three groups (table 2) showed that mean serum triglyceride levels, 199 mmol/l, resulted higher to group 3 of PIH women compared to 139 mmol/l and 145 mmol/l in the group 1 (control) and healthy pregnant women, group 2. There was statistically significant difference in the mean total cholesterol across the 3 groups ($p<0.001$), though the values in the groups 2 and 3 were higher compared to group 1. Regarding to LDL-cholesterol levels the values were statistically significant between three groups. Mean HDL-cholesterol values was lowest in women with preeclampsia, 50 mmol/l compared to group 1 and 2, ($p<0.001$).

Correlation analysis between serum lipids and diastolic blood pressure showed HDL-cholesterol having a statistically significant, negative correlation ($r=.0.446$) ($p<0.001$) with diastolic blood pressure decreases positively with diastolic blood pressure ($r=0.257$, $r=0.256$, $r=0.56$) respectively which was not statistically significant ($p>0.001$). Gestational age had a statistically significant correlation with total cholesterol ($r=0.550$; $p<0.001$) with increasing gestational age. The total cholesterol values increased.

Table 1: Demographic characteristics of respondents by study group

Parameter	Women with PIH	Healthy pregnant women	Controls
Total number of subjects (n)	26 (100%)	68 (100%)	28 (100%)
Mean BMI (kg/m^2)	26.6	24.4	24.2
Mean age (years)	30.8	27.5	27.4
Mean systolic blood pressure (mmHg)	138	112	110
Mean diastolic blood pressure (mmHg)	84	75	76
Mean period of gestation (weeks)	30	26	0

Table 2: Lipid profile, mean values, in normotensive non-pregnant, normotensive pregnant and women with pregnancy-induced hypertension.

Parameter	Control	Healthy pregnant women	Women with PIH	p-value	Remark
Triglyceride (mmol)	139*	145	199	<0.001†	Statistically significant
Total cholesterol (mmol)	178	187	299	<0.001	Statistically significant
LDL cholesterol	92	103	138	<0.001	Statistically significant
HDL cholesterol	61	54	50	<0.001	Statistically significant

* Mean value of selected parameter.

† P-value from the General Linear Model.

4. DISCUSSION

The role of lipid metabolism on the development of preeclampsia is of great interest for the physicians involved in the area. Previous studies have reported that plasma lipid levels were higher in pre-eclamptic pregnant women compared to healthy pregnant women (Kokia *et al*., 1990; Ware Jauregui and Sanches 1999). It is thought that lipid changes have a role on endothelial cell damage (Flahavan, 1992), which is a characteristic symptom in preeclampsia. Oxidized LDL inhibits endothelial prostacyclin synthesis and inactivates the Endothelial Derived Relaxing Factor EDRF (Gratacos *et al*., 2003). It is assumed that oxidized LDL, also stimulates synthesis and release of endothelin, a natriuretic hormone, which has vascular smooth muscle contracting effect (Rifkind and Levy 1937; Robson 1999; Stewart and Monge1993). These changes cause

thrombocyte activation that result in thromboxane release which leads vasospasm (Redman, 1991).

(Ozgur *et al*., 2008) demonstrated raised triglyceride and VLDL-levels in the aetiopathogenesis of women with mild and severe pre-eclampsia. (Ware Jauregui *et al*., 1999) have reported high TG and low levels of HDL in pre-eclamptic patients compared with control groups in their study. In their study (Michail *et al*., 1995) have demonstrated triglyceride levels to be high in mild pre-eclampsia group, but similar in severe pre-eclampsia group compared to control group and defended that no direct relation exists between TG level and severity of preeclampsia.

Total cholesterol values were higher in women with pregnancy induced hypertension and normotensive pregnant women than in controls in this study, though the difference was not statistically significant. (Baksu *et al*., 2005) found that total cholesterol levels were similar in preeclampsia and control groups, while (Ozgur *et al*., 2008) reported that cholesterol levels were similar in both preeclampsia and non-pregnant women, while the levels were higher in the cases of severe pre-eclampsia. LDL levels were similar across the 3 studies groups, just like the finding by (Baksu *et al*., 2005).

HDL levels were lowest in women with pregnancy induced hypertension, compared with pregnant and non-pregnant women. The difference was not statistically significant (Enquobahrie *et al*., 2004).

Similarly, Jayantha et al., (2006) reported a decrease of HDL cholesterol concentration in women with preeclampsia. In addition, Asaolu *et al*., (2010) demonstrated low levels of HDL and LDL in pregnant women with hypertension. HDL-cholesterol showed a statistically significant correlation with diastolic blood pressure.

5. CONCLUSIONS

In the present investigation, there was mild hypertriglyceridemia in women with pregnancy induced hypertension, with HDL-cholesterol being lowest in this group of women and correlating negatively with diastolic blood pressure. Cholesterol levels correlated positively with increasing gestational age, with LDL and total cholesterol also correlating weakly with diastolic blood pressure, all this are a pioneer to fact that dyslipidemia may play a role in aetiopathogenesis of pregnancy induced hypertension.

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OPERATIONS BREAKDOWN AND PUTTING THE PRODUCTION TARGETS IN CLOTHING INDUSTRY

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ABSTRACT

Production targets are of great importance for the management system as it allows for a better use of human and material resources. Consequently, work can be performed as efficiently as possible. A good management is undoubtedly related to time table and continuous training of employees. Production targets are carried out by putting operations breakdown and time measurement of every work operation to establish standard minute value. Standard minute value is the time allocated to an individual to perform a particular operation or process. Time measurement consists of description of work systems, especially of processes, methods, work conditions and the level of performance.
Keyword: production targets, operations breakdown, time measurement.

1. INTRODUCTION

Work measurement is the application of techniques designed to establish the time for a qualified worker/process to carry out a task at a defined speed (Louis Armendariz 2009).

Production targets are important for the organization of work and the use of human and material resources in a rational way (Belakova *et al.*, 2006). In addition, they are closely related to the increase of work performance and creation of best conditions for applying work principles and reward on basis of quality and quantity performance (Llaci *et al.*, 2001).

Every company can set up its own production targets. However, some production processes are inapplicable due to complexity of the technology used. Continuous monitoring of production targets and controlling of their application is the main responsibility of any reliable manager (Nakuçi *et al* 2002).

The present investigation is carried out in a company in Tirana, Albania which produces sportswear operating in full package. The main customers are French and Dutch.

2. MATERIALS AND METHODS

In the present investigation a sport blouse was involved and the following procedures were carried out: i) operations of production breakdown and, ii) 10 consecutive measurements for each operation. A qualified operator was used to measure every work operation of employees (USAID, 2011).

Work is measured by: i) recording observed time, ii) assessing the performance of operator (BSI scale-Rating of work), iii) calculating basic minutes, iv) allowance and, v) calculating standard minutes (USAID, 2011).

Luis Armendariz (2009) stated that work measurements are a means to address: i) establishing the standard time for a task, ii) optimizing employee levels and, iii) planning and controlling the production.

A stopwatch was used to measure time (Spahija *et al*., 2010) and the data were recorded in the time sheet. Operator performance is assessed using the BSI scale (rates of working).

Assessment of operator performance is one of the most difficult skills for an industrial engineer to acquire and takes a lot of practice in order to become consistent. The assessment or rating of an operator performance is used to adjust the observed time either up or down to what Industrial Engineer believes a standard operator would be able to achieve (Khatun, 2013).

"Standard Performance" is defined as the output that a qualified (fully trained) and motivated operator can achieve over length of the working day/shift using specified method and meeting the required level of quality (Zuradaih *et al*., 2014). The time taken (observed time) is multiplied by the rating (using 0-100 scale) to give the basic minutes for an operation. The basic minutes than can be adjusted by the addition of allowances to give a standard minute value. (USAID, 2011)

There are two types of allowances: i) contingency allowances given to compensate the operator for interruptions occurring during the normal completing of an operation. Interruption consists of changing of the threads and bobbins and, ii) personal allowances given to compensate the operator for fatigue and breaks. However, it is a subject to the policy of the company (Zielinski *et al*., 2006).

3. RESULTS

Once the product arrives in the production line, its quality is investigated and the breakdown of products operations occurs.

Fig. 1. The sports blouse.

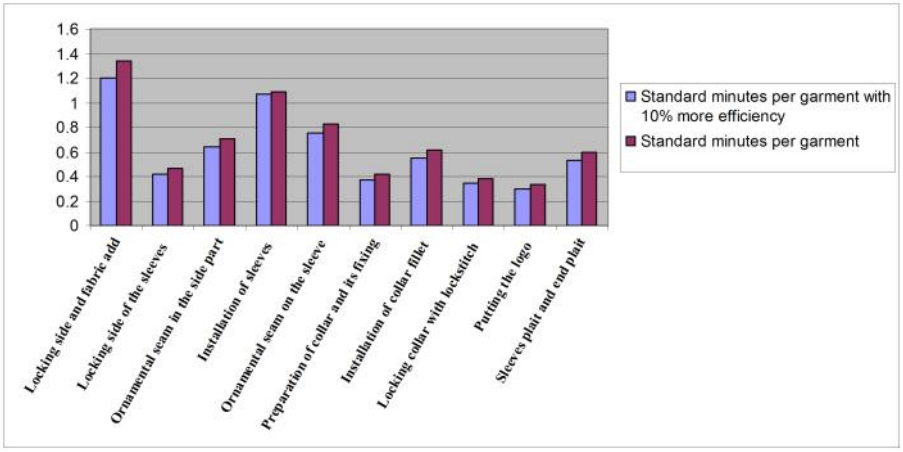
The production of a dacar blouse passes through the following operations: i) Locking side and fabric add in the back, ii) locking side of the sleeves, iii) ornamental seam in the side part, iv) installation of sleeves, v) ornamental seam on the sleeves, vi) preparation of collar and its fixing, vii) installation of collar fillet, viii) locking collar with lockstitch, ix) setting the logo and, x) sleeves plait and the end plait.

The calculation of production targets is made based on table 1 (time study observation sheet), considering the allowances, using the stopwatch and the BSI scale (rates of work)(bsi group). The average minutes per cycle are multiplied by rating for every process, which gives Normal minutes per cycle. Standard minutes per GRMT (garment) are a summary of Normal minutes per cycle with relaxation and contingency allowances. Standard minutes values are used to: i) set individual/line targets, ii) calculate individual/line/factory efficiency, iii) balance the processes, iv) plan the production and, v) calculate the cost.

Table 1. Time study observation sheet

The study observation sheet									**Date:**	
Style: Dacar Blouse										**Sheet no:**
Operator: Time Finished: Time Started:	RELAXATION AND CONTIGENCY ALLOWANCES: 7%									
Elapsed time:										
Recorded time:										
Operation	Observed minutes per cycle					Average min per cycle	Rating	Norm minutes per cycle	Basic mins per GRMT	Standard mins per GRMT
Locking side and fabric add	1.71	1.66	1.68	1.75	1.65					
	1.66	1.71	1.75	1.65	1.66	1.68	75	1.266	1.688	1.336
Locking side of the sleeves	0.6	0.58	0.58	0.56	0.55					
	0.58	0.56	0.6	0.55	0.56	0.57	70	0.399	0.57	0.469
Ornamental seam in the side part	0.81	0.81	0.8	0.8	0.78					
	0.78	0.81	0.8	0.81	0.8	0.8	80	0.64	0.8	0.71
Installation of sleeves	1.28	1.31	1.28	1.25	1.25					
	1.26	1.3	1.28	1.25	1.25	1.272	80	1.0176	1.272	1.0876
Ornamental seam of the sleeves	0.93	0.91	0.91	0.88	0.88					
	0.91	0.88	0.91	0.93	0.9	0.94	85	0.7684	0.904	0.8384
Preparation of collar and its fixing	0.48	0.46	0.46	0.45	0.5					
	0.48	0.45	0.46	0.48	0.45	0.467	75	0.35025	0.467	0.42025
Installation of collar fillet	0.68	0.71	0.66	0.7	0.63					
	0.68	0.7	0.7	0.65	0.66	0.677	80	0.5416	0.677	0.6116
Locking collar with lockstitch	0.48	0.46	0.5	0.51	0.45					
	0.45	0.46	0.48	0.5	0.5	0.479	65	0.31135	0.479	0.38135
Putting the logo	0.3	0.36	0.33	0.31	0.38					
	03.86	0.31	0.33	0.31	0.36	0.355	80	0.268	0.335	0.338
Sleeves and plait and end plait	0.68	0.7	0.75	0.71	0.66					
	0.68	0.7	0.73	0.7	0.71	0.702	75	0.5265	0.702	0.5965
Total standard minutes						7.894		6.0887	7.894	6.7887

The table shows a low level of performance for every process which is reflected to high values of standard minutes per garment for every process (the last column of the table). If the efficiency of the operator increases (the operator works faster), we could have different values of average minutes per cycle and lower values of standard minutes per garment, i.e., more output could be produced within a short period of time. The graph 1 shows the differences in time for every process using standard minutes per garment (last column of table 1) and of standard minutes per garment if the operators work with 10% more efficiency.



Graph 1. Time for every process

The quantity of blouses that the production line can produce is 60 pieces a day. If the operators work with 10% more efficiency, the production line could produce 8 pieces more in a day.

This value will be more considerable if the quantity of the product ordered is high.

4. CONCLUSIONS

Performance appraisal system is of great benefit for any company. Developing and implementing an effective appraisal system is no easy task, however. There are three major steps in the performance appraisal process: identification, measurement, and management. With identification, the behaviors necessary for successful performance are determined. Measurement involves choosing the appropriate instrument for appraisal and assessing performance. Management, which is the ultimate goal, is the *reinforcing* of good performance and the correction of poor performance.

It is recommended that the operator should always be aware of the level of performance and the level of output required; he/she should have sufficient and continuity of work for the whole shift/day; the machine should work properly, the operator should use the correct handling method; the workplace should laid effectively; the operator should require additional training on a different operation or equipment

By achieving an improved level of performance and by working at their full potential, the operator will benefit from increased salary.

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PHYSICO-CHEMICAL FEATURES OF COASTAL AQUATIC ECOSYSTEM OF NARTA LAGOON IN ALBANIA

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ABSTRACT

Situated in the south-west of Albania, Narta Lagoon is the second largest lagoon and one of the most important sites in the country. The lagoon is mentioned for its amazing biodiversity. In the present paper, physico-chemical parameters of water in the Narta Lagoon such as pH, transparency, temperature, BOD, COD, NO_3-N, NO_2-N, NH_4-N, P-PO_4 and P total are investigated. Samples were collected from 8 sites, respectively in the Lagoon and in the sea, four times 4 times a year throughout the investigation period. Results reported that: i) the level of physico-chemical parameters is the same at all the sites, ii) the anthropogenic activity affects greatly the dissolved oxygen and nutrients (nitrogen and phosphorus). The data in the present investigation collected are quite variable. However, information about the impact of anthropogenic activity on the inland waters that flow in the lagoon could be reported and, iii) the trophic state indexes (TSI), total phosphorus and the transparency (Secchi disc) define the mesotrophic state of the Lagoon.

Keywords: Narta Lagoon, Albanian wetlands, water quality, trophic index, mesotrophy

1. INTRODUCTION

Aquatic ecosystems are characterized by large variation in abiotic variables and of species assemblages, as well as by unpredictable changes in time and space (Basset *et al.*, 2001).

In the coastal zone, aquatic ecosystems are mainly regulated by physical processes related to freshwater and seawater flow. Freshwater flow into coastal

aquatic systems occurs very irregularly, both in time and intensity, whereas sea flows are much more regular in time although irregular in intensity (Carter 1988). In any case, it is the mixing of these two major forces that mostly regulates the functioning of coastal aquatic ecosystems (Nixon 1982). As a consequence, a wide range of environmental conditions must be expected for any aquatic coastal ecosystems and may be represented while studying aquatic ecosystems along any single coast (Guelorget and Perthuisot 1983).

Coastal lagoons located between land and sea are influenced by both the marine and terrestrial environments. Coastal lagoons are naturally enriched areas with very unstable environmental conditions due to their confinement from the open sea and to their shallowness. In this sense they are considered as naturally stressed environments. Furthermore, being close to land, they are vulnerable to human disturbance (Bellan 1972; Stora and Arnoux 1983; Reizopoulou and Nicolaidou 2004).

Narta Lagoon, one of largest lagoons in Albania with an area of 2,773 ha (Lami, 2004) is located (40°32'N; 19°28'E) to the north-west of Vlora city, by the Adriatic Sea. Its depth varies from 0.70–1.50 m, and the lagoon is connected to the sea through canals in the north and south (Shehu and Shabani, 2010). Anthropogenic activity such as intensive fishing, industrial discharges, inland drainage, urban sewage and has been of great impact for the ecosystem of the Narta Lagoon (Pano 1992; Phare 2002). Despite relatively big surface the lagoon is characterized by short-term water circulation events because of: i) the huge water inflow and outflow through water exchange between lagoon and sea and, ii) its small depth. In addition, wind, air temperature, and pressure and bottom friction affect water movement of the lake.

2. MATERIALS AND METHODS

Sampling area

Investigation of the water quality in the Lagoon has been carried out in the framework of the project implementation "Preservation of the coastal and wetlands in the Mediterranean Region" (Sanxhaku *et al.*, 2003; Technical report 2003; WB 2004). Depicted in figure 1, samples were collected from 4 sampling sites within the lagoon and 4 sampling sites in the sea, four times a year throughout the investigation period. The sampling sites in the sea are: in front of first lagoon's channel (station 1), in front of ex-oil platform (station 2), behind the platform zone (station 3) and, in front of the second lagoon channel (station 4).

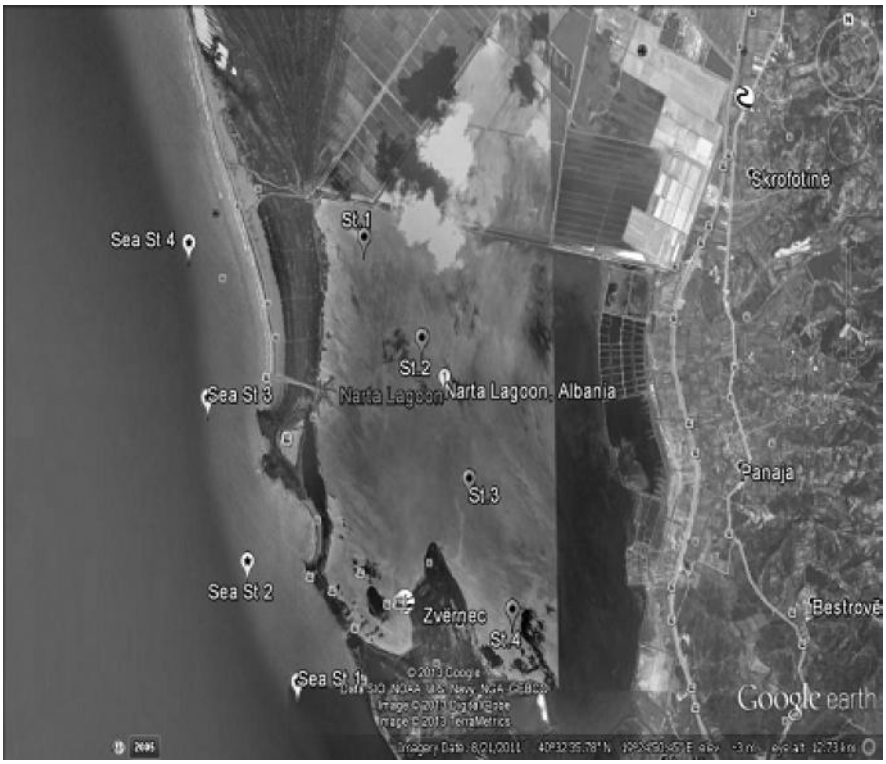

Fig. 1. Location of the sample sites.

Methods of analyses

Collected from the surface and using using 3L Niskin bottles filtered through HA Millipore, 0.45 μm, water sampling was based on sampling procedures for the shallow waters (Strickland and Parsons 1992**).** Physico-chemical parameters such as pH, transparency, temperature, BOD, NO_3-N, NO_2-N, NH_4-N, P-PO_4 and P total were investigated (APHA 1998; Sanxhaku and Selfo 2005). Once collected, the samples were transported at the laboratory in cooling box at 4ºC. Sampling, transporting and conservation were in line with the ISO standards and the EU and APHA recommendations (Bartram and Balance 1996). These procedures are validated for the quality control and assurance is applied to data according to the procedure of internal quality (Lund *et al.*, 2001). Fifty-two samples were collected from 2007- 2010 and analyzed. The trophic state of a lake (Carlson and Simpson, 1996) could be determined based on phosphorus amount inside the lagoon. Meanwhile the transparency levels taken by Secchi disk measurements can be used as index of trophic state of a lake.

3. RESULTS AND DISCUSSION

Phosphorous concentration depends on biological activity and the flow rate of the water. Results report that spring marks the highest concentration rate (from 0.012 to 0.025 mg/l P) and winter marks the lowest concentration rate (from 0.007 to 0.010 mg/l P). The level of orthophosphate varies from 0.007 to 0.025 mg/l P in all the sites (fig.2).

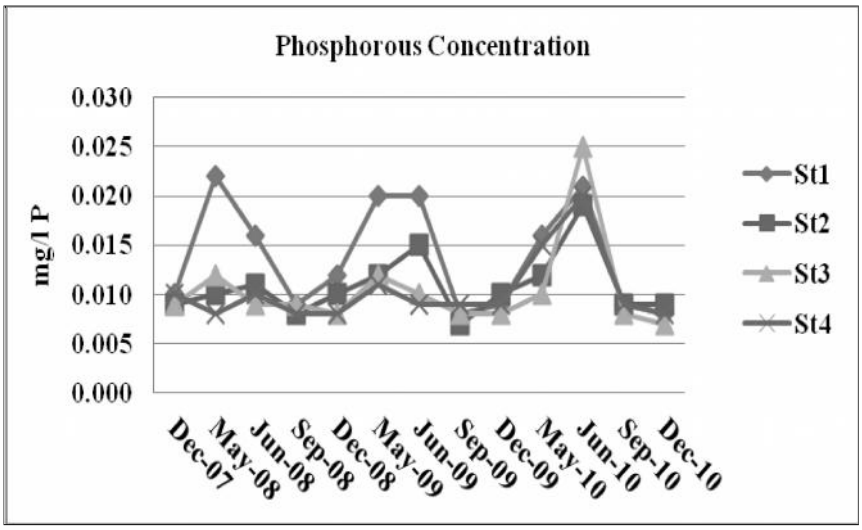

Fig. 2. Tendency of phosphates concentration.

Nitrogen fixation, nitrification and denitrification are critical steps of the nitrogen cycle, the first being an input and the latter a loss of nitrogen from the system (Herbert 1999; Nedwell *et al*., 1999; Welsh 2000). Nitrogen concentration as ammonium, nitrate or nitrite is closely related with the nitrogen cycle. The time distribution of this indicator in the lagoon water follows that of water circulation from the water exchange between sea and lagoon, accompanied with organic development during the summer period when the temperature is higher and the water warmer, giving the possibility to algae or other biotic organism to develop and change the equilibrium between live organisms and the nitrogen concentration in water (Kormas 2001). Results reported that the nitrate level in the water samples ranges from 0.1 mg/l to 0.66 mg/l in all the sites of Narta Lagoon. In addition, a slight tendency of decrease for the nitrogen during the wet period of the year is reported (fig.3).

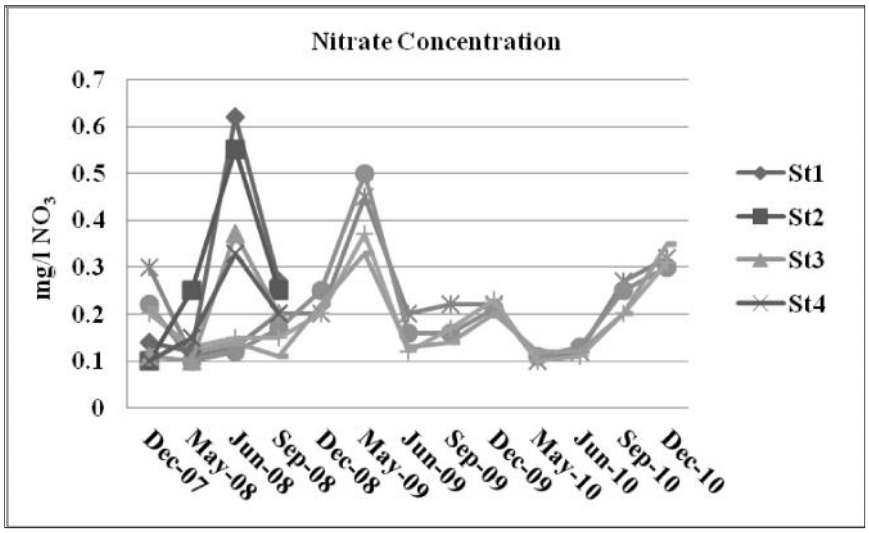

Fig.3. Tendency of Nitrates concentration.

Biological oxygen demand (BOD) is one of the most common generic indices used to assess the total organic pollution load of waters contaminated by reductive pollutants. Generally BOD increases in springtime. Different sites have different values of BOD-— varying from 1 to 6 mg/l O_2-— due to water staying in lagoon, the population of the organism near the sites and polluted waters coming from the fresh water channels (fig.4).

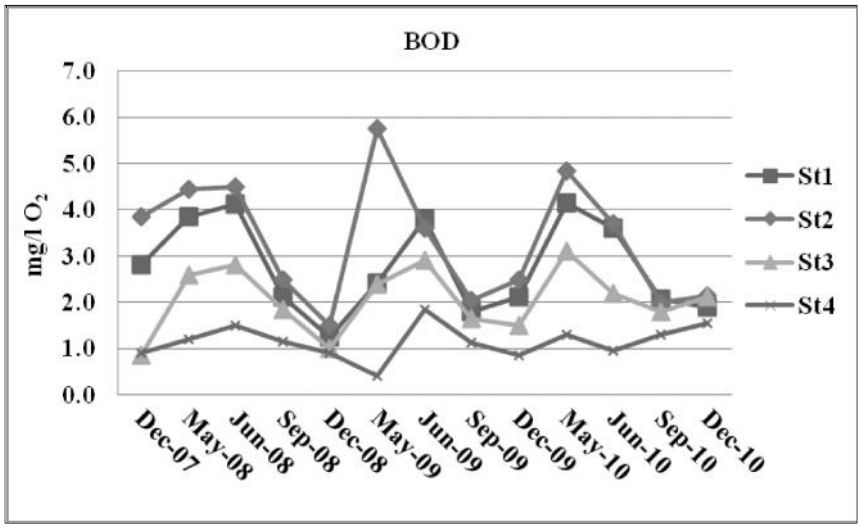

Fig. 4. Tendency of BOD content in surface water.

The concentration of dissolved oxygen is subject of the photosynthetic activity and fresh water discharge as well from the fresh waters (coming from the channel of inland water discharges) into the lagoon. The water in the Narta Lagoon is saturated with oxygen, in spite of domestic inflow and some industrial wastewaters. This indicator varies from 7.17 to 10.07 mg/l. (fig.5). All these data report that the water in the lagoon has a rapid mix with fresh water coming from inland channels or from sea water exchange in communication channels.

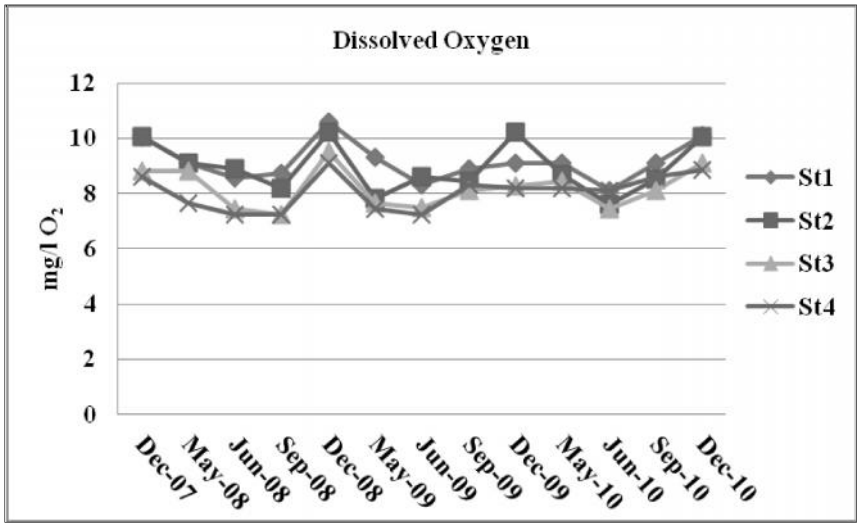

Fig. 5. Oxygen concentration distribution in different stations.

Trophic Classification

Transitional waters are very vulnerable to eutrophication and microbial and chemical pollution because of their confinement, shallow depth and reduced water exchange (Barnes 1999).

Eutrophication is the process by which water bodied are enriched with nutrients, increasing the production of rooted aquatic plants and algae (Basset *et al*., 2001). Upon Carlson classification a lake or a lagoon is usually classified in one of three classes: oligotrophic, mesotrophic or eutrophic. Oligotrophic water bodies generally host very little or no aquatic vegetation and are relatively clear, mesotrophic water bodies show moderate levels of nutrients and chlorophyll, while eutrophic water bodies tend to host large quantities of organisms, including algal blooms (Lucena *et al*., 2001). Water bodies with extreme trophic indices may also be considered hyperoligotrophic or hypereutrophic. Table 1 demonstrates how the index values are translated into trophic classes.

Table 1. Relationships between Trophic Index (TI), chlorphyll (Chl μg/l), phosphorus (P μg/l), Secchi disc (SD, m), and Trophic Class

TI	Chl	P	SD	Trophic Class
<30—40	0—2.6	0—12	>8—4	Oligotrophic
40—50	2.6—7.3	12—24	4—2	Mesotrophic
50—70	7.3—56	24—96	2—0.5	Eutrophic
70—100+	56—155+	96—384+	0.5—<0.25	Hypereutrophic

Phosphorus indices report that the Narta Lagoon belongs to the mesotrophic state (fig. 6).

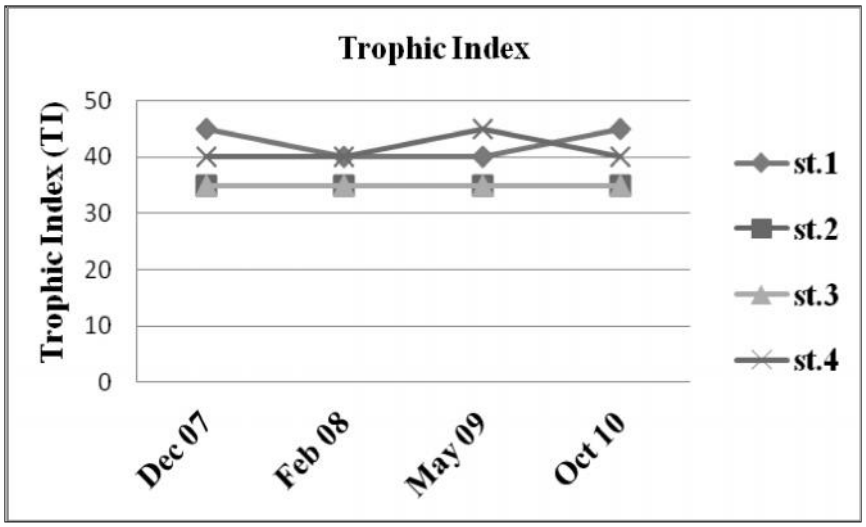

Fig. 6. Tendency of Trophic Index in Narta Lagoon water.

This index is the same only for the sites in the center of the lagoon where the mixing process is very fast and the turnover of the water is made in a short time. Meanwhile in the other stations this index is different. This reports a delay in the mixture of the water and the resident time for the microorganism is longer than in the other part of lagoon.

These indicators of the water quality are at the same level throughout the year, even in the sea waters outside the Narta Lagoon.

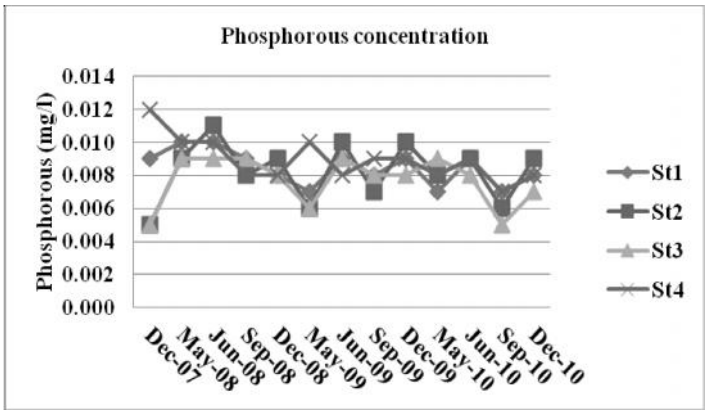

Fig. 7. Phosphorous concentration in coastal waters.

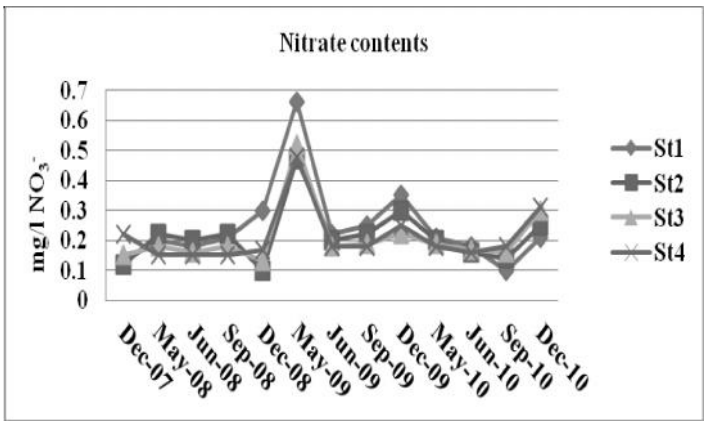

Fig 8. Nitrates concentration in coastal waters.

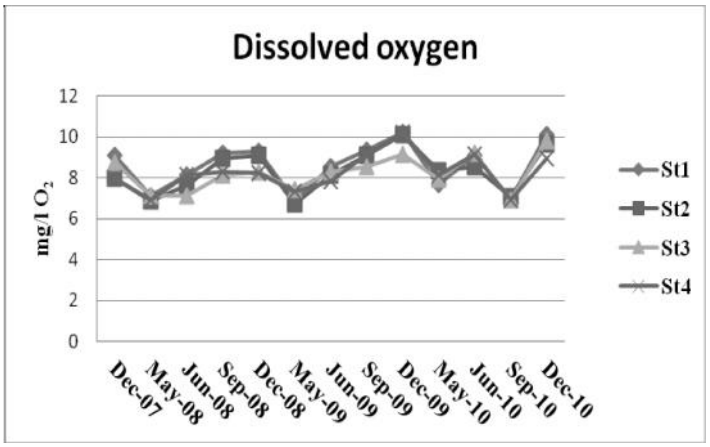

Fig 9. Oxygen concentration in coastal waters.

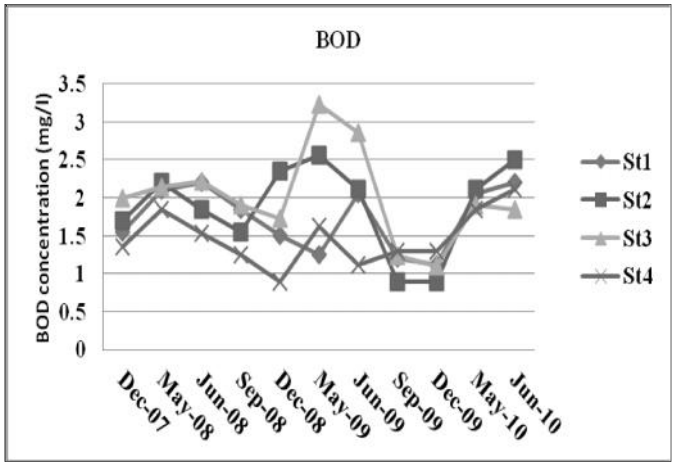

Fig 10. BOD content in coastal waters.

By comparing of the respectively values of the analyzed physico-chemical parameters (BOD, O.D, NO_3-N, P-PO_4) on the coastal stations is observed the seam similar trend (figure 7-10).

Sampling data for both phosphorus and Secchi disk show that the coastal waters outside of the Narta Lagoon belongs to the oligotrophic state (figure 11).

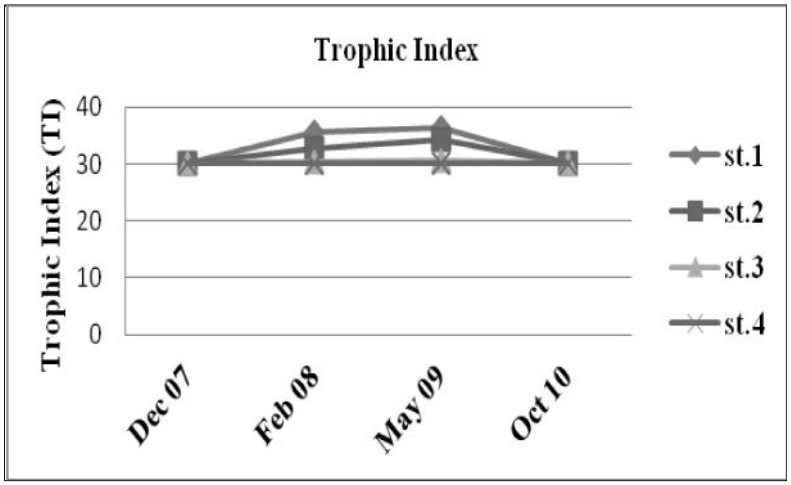

Fig. 11. Tendency of Trophic Index in costal water.

This index is the same for the coastal sites in north of the main communication channel between the sea and lagoon. This means that the waters that come out from the lagoon mix quickly and they seem to increase the index values in other coastal sites.

4. CONCLUSIONS

In the present investigation the following conclusions are drawn: i) considered of good quality for the fish species, regardless level of phosphorous and nitrates, the quality of the water in the Narta Lagoon is different in different parts of it, ii) continuous discharges are of a negative impact for the flora and fauna of the lagoon and a threat for the population living in the surrounding area, iii) based on the trophic indexes (TI) and the data of total phosphorus indices, the Lagoon belongs to the mesotrophic state, iv) based on the trophic indexes (TI), Sampling data for both phosphorus and Secchi disk transparency show that the coastal waters outside of the Lagoon belong to the oligotrophic state and, v) the sites have different values of physico-chemical parameters..

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ASSOCIATION FOR MEDICINAL AND AROMATIC PLANTS OF SOUTHEAST EUROPEAN COUNTRIES GIVES A MAJOR BOOST TO SCIENTIFIC RESEARCH AND ITS APPLICATION IN THE ECONOMY

The 8th International Conference on Medicinal and Aromatic Plants of the Southeast European Countries was organized in Durrës and it is hoped that holding such a prestigious event will do much to promote the importance of this science area to the economic development of the country.

This conference in Durrës from 19 – 22 May 2014 was the first event of its kind organized in Albania by the Association for Medicinal and Aromatic Plants of Southeast European Countries (AMAPSEEC), Albanian Academy of Sciences and Agricultural University of Tirana welcomed participants from South-Eastern European Countries and beyond. The association consists of the most eminent personalities from the 16 South-eastern European Countries and more than 500 members from other countries. The Albanian Academy of Sciences, the National Academy of Sciences in the country and the most important science institution supported this conference.

The primary objective of AMAPSEEC is the future of medicinal and aromatic plants. Consequently, it aims to invest in future scientific leaders and in innovation; influence properly policy making with the best scientific advice and invigorate this scientific field and further education in the area. In addition, it aims to increase access to the best scientific solutions. Many of the issues tackled are global in nature and require collaboration among scientists. Every biennial meeting, it is discussed on current technologies, as innovation is a tool to address sustainable development. The backbone of AMAPSEED is active participation and a sincere and concrete collaboration among participants for the benefit of society.

A list of guests that included the Minister of Education and Sports, Mrs. Lindita Nikolla, Deputy Minister of Agriculture, Rural Development and Water Administration, Mr. Alban Zusi, Academician Prof. Dr. Nazim Gruda, members of the Albanian parliament and many representatives of higher education and research institutions, demonstrated the rising awareness of the importance of this science to Albania's economic and scientific development. The main topics

of the conference were: Biodiversity, management and conservation; Biotechnology and molecular biology; Cultivation, breeding and industrial processing; Phytochemistry, pharmacognosy, ethnopharmacology, pharmacology and toxicology and, Quality control and management, which show the weight of such studies to different disciplines and the necessity of the development of this science area.

Of great interest were the scientific presentations held by Prof. Máthé and Prof. Pieroni. Prof. Akos Máthé estimated the tendencies, possibilities and challenges arisen during the research and emphasized the importance of cultivation of aromatic and medicinal plants. In addition, he paid a great attention to the application of international standards (GAP, GACP, Fairwildand certifications) for the production of plants. Production of high quality plants is closely related with the technologies applied in the area of biotechnology and analytical methods used which can easily identify the falsified products. Andrea Pieroni, an Associate Professor of food botany, ethnobotany and ethnobiology at the University of Gastronomic Sciences in Pollenzo, Italy demonstrated the importance of scientific research in the area of local and traditional food, the use of medical plants and the concepts related to "terroir". He stated that the Balkans is mentioned for the unique biodiversity and diversity of culture which coexist and co-evaluate. Moreover, he showed some examples of coexistence and co-evolution from northern and eastern Albania, and Romania.

Some other researchers such as Assoc. Prof. Baricevic, Prof. Zora Dajiç, Prof. Assoc. Ibraliu etc. provided very interesting information about the conservation of these plants as a tool to address the wellness of future generation. Acad. Assoc. Prof. Kongjika and her collaborators reported the results about the molecular, biochemical characterization, *in vitro* conservation of some Albanian populations of sage and the evaluation of optimal sage chemotypes. This study contributes to the use of scientific methods for creating new genetic forms of sage, based on native ecotypes with high productivity and quality.

The participants were informed about the activity of Albanian private enterprises involved in the area of aromatic and medicinal plants. They visited the XHERDO'S HERBS, a company that is involved in the elaboration and export of these plants (semi-finished), and essential oil. The Salvia Nord Co. is involved in the cultivation of lavandula, thymus, rosemary and sage.

There were about 250 scientific presentations, including 7 presentations from invited speakers, 32 introductory plenary and oral lectures and 233 poster presentations. The papers were prepared by scientists and experts from Albania, Italy, Slovakia, Serbia, Bulgaria, Hungary, Slovenia, Croatia, Kosovo, Montenegro, the Former Yugoslav Republic of Macedonia, Bosnia and Herzegovina and many other European countries. Moreover, institutions from

Asia, Africa and United States of America played a key role in the conference.

The Conference was generously supported by USAID Assist and IMPACT under the framework programme Albanian Agriculture Competitiveness Lushnja.

In the end a chart with recommendations was drafted to increase access to the best scientific solution for the benefit of respective AMASEEC member countries and the region itself.

DIRECTORY OF MARINE GEOLOGY (BRIEF COMMUNICATION)

The Directory of Marine Geology of the Albanian Geological Survey has been currently founded. The official foundation date of the Directory of Marine Geology of the Albanian Geological Survey is 1 July 2014, when the Ministerial Council met on April 23, 2014 decided to found it. Doctor Arben Pambuku was elected Head of the Directory of Marine Geology.

The mission of the directory is to recognise, promote, and support excellence in science and to encourage the development and use of science for the benefit of society in Albania.

Its priorities are: i) promoting science and its benefits, ii) recognising excellence in science, ii) supporting outstanding science, iii) providing scientific advice for policy, iv) fostering international and global cooperation and, iv) education and public engagement.

The Directory is engaged in compiling Marine Geology maps at scale 1:50 000, investigating the lithological composition of the substrate, bathymetric changes and seabed morphology, identifying natural resources in sea and coastal zones, studying of "dependant ecosystems", relationships between river's deltas, surface water, groundwater, wetlands and seas, facilitating the investigation of harbours, quays construction and other engineering works throughout the coast, monitoring the coastline and erosion-accumulation rate, cooperating in the area of archaeological research in the framework of the conservation of marine biodiversity, running off and coordinating science activities field of coral ecosystems, karstic underwater caves and beaches and oversee their developing process, investigating freshwater submarine sources, developing a national database for marine studies and data, cooperating in national and international projects for the realization of marine studies on the geology of the substrate, seismic risk, marine tectonic aspects, coastal dynamics connection with tectonic activity, etc. and, providing information about the possibility of the presence of oil-and gas structures into the sea.